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# HOME ECONOMICS



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# THE JOURNAL OF THE Society of Dyers and Colourists

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## Proceedings of the Society

### LEEDS JUNIOR BRANCH

Meeting held at the University of Leeds, on 18th October 1949, Professor W. BRADLEY in the chair

## Recent Trends in the Search for New Azo Dyes

### II—Dyes for Acetate Rayon and Nylon

A. H. KNIGHT

#### Dyes for Acetate Rayon

The early history of the development of dyes for cellulose acetate rayon is now generally well known. It will be recalled that, when this fibre was marketed after the first world war, very few of the then existing commercial acid wool and direct cotton water-soluble dyes, which for the most part depended for their water solubility on the presence of nuclear sulpho groups, had any affinity for it. Certain insoluble aminoazo and hydroxyazo compounds, as well as certain nitro compounds such as nitrodiphenylamines, were found by Clavel to have affinity for the new fibre<sup>1</sup>. Pioneer work in Britain by British Dyestuffs Corporation Ltd. (now part of Imperial Chemical Industries Ltd. (ICI)) and British Celanese Ltd. (BrC) led to the first special ranges of dyes for this material. The Ionamine dyes<sup>2</sup> of the former firm, discovered by A. G. Green and K. H. Saunders, were temporarily solubilised aminoazo and aminanthraquinone compounds which had no affinity for cotton or other purely cellulosic fibres. Solubilisation was effected by means of an *N*-sulphomethyl group. In the case of the azo dyes this group was usually introduced into the coupling intermediate by reaction of a primary or secondary coupling amine with formaldehyde and sodium bisulphite. It hydrolysed in the hot dye bath, under slightly acid or slightly alkaline conditions, regenerating the parent insoluble compound in finely divided form suitable for uptake by the fibre. The S.R.A. (BrC) dyes were dispersions of aminoazo- and hydroxyazo-benzene derivatives and of some nitrodiphenylamines, the dispersing agent being sulphoricinoleic acid. British Dyestuffs Corpn. also marketed dispersed products of these types under the name of Dispersol colours. The pioneering phase of the development of dyes for acetate rayon was concluded by the discovery by Baddiley and Shepherdson of this firm of the Duranol dyes. These were dispersed aminanthraquinone derivatives which yielded hues from orange to blue of a brilliancy and

light fastness not generally achieved by the azo products thus far discovered, the violets and blues being especially important in the absence of any suitable direct dyeing azo products for these colours.

By the late 1920s most of the important dye-makers of Europe and America had entered this field of dye manufacture, and effort was concentrated on the development of ranges of dispersed dyes, first as pastes, then as powders. Thus there were developed, in addition to the initial members of the Dispersol and Duranol ranges, the first members of Continental ranges such as the Cellitons (IG), the Setacyls (Gy), the Artisils (S), and the Cibacets (Ciba), to name a few of the competitive ranges. New members were added from time to time, and by the outbreak of the recent war dischargeable water-insoluble azo products ranging from yellow to blue and of good brightness were available. The yellow to red and orange-brown dyes had in general good light fastness, but the violets and blues were only moderate in this respect. Brighter dyes, faster-to-light violets and blues as well as green dyes, were catered for, as already indicated, by anthraquinone derivatives which were not dischargeable. Blacks were obtained by diazotisation of certain aminoazo compounds, e.g. 4-amino-4'-dimethylaminoazo-benzene (Dispersol Diazo Black A), on the fibre and coupling with 2:3-hydroxynaphthoic acid.

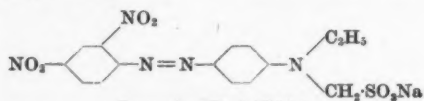
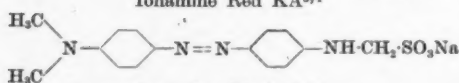
#### IONAMINE DYES

The Ionamine dyes were useful for a time, as they could be applied in a somewhat similar manner to direct cotton dyes, giving fairly good penetration of the fabric. They suffered, however, from the defect of hydrolysing at different rates, which made their use in mixtures somewhat unsatisfactory, thereby creating difficulties in matching. The colours of the final dyeings were also different from those of the original dye solutions, owing to the hypsochromic effect associated with the loss of the

alkyl group carrying the solubilising group. The range of hues available and light fastness properties were also limited. Examples which may be cited are—

Ionamine Yellow MA<sup>3</sup>

which gave reds by diazotisation on the fibre and development with  $\beta$ -naphthol or 2:3-hydroxy-naphthoic acid.

Ionamine Red KA<sup>3,4</sup>Ionamine Black A<sup>3,4</sup>

which gave yellows directly and was used commercially for blacks obtained by diazotisation on the fibre and development with 2:3-hydroxy-naphthoic acid.

#### DISPERSED WATER-INSOLUBLE DYES

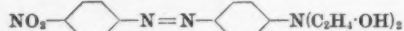
Yellows were provided by structures such as—

Aniline  $\rightarrow$  2:4-dihydroxyquinoline (Dispersol Yellow 3G)<sup>5</sup>

*m*-Nitroaniline  $\rightarrow$  4-hydroxy-*N*-methyl-2-quinolone (Celliton Yellow 5G)<sup>6</sup>

and *p*-Aminoacetanilide  $\rightarrow$  *p*-cresol (Celliton Fast Yellow 6G)<sup>6</sup>

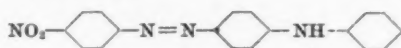
The use of orange secondary diazo dyes of the class A  $\rightarrow$  M  $\rightarrow$  phenol was patented by British Celanese Ltd.<sup>7</sup> and Celliton Fast Yellow 5R (*p*-aminoazobenzene  $\rightarrow$  *o*-cresol)<sup>8</sup> is an example of this class. A large number of dyes ranging from orange to blue were built up by appropriate substitution of 4-nitro-4'-aminoazobenzene (Celliton Fast Orange GR)<sup>6</sup>. Substitution of the 2 and 2:6 positions in the latter compound with one or other of the halogen, nitro, and cyano groups; of the 2' and 2':5' positions by one or other of methyl, methoxy, chlorine, and acetyl amino groups; as well as of the 4'-amino group by alkyl, hydroxyalkyl, alkoxyalkyl, cyanoalkyl, aryl, or aralkyl groups, played a very important part in the researches leading to the development of members of deeper colour for the commercial ranges of dispersed dyes. Particularly important were dyes built up on the pattern of Dispersol Fast Red R<sup>9,10</sup>—



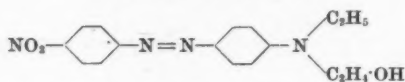
which was first described by Green and Saunders<sup>9</sup> in 1923 in their search for water-soluble dyes for acetate rayon. At that time it was found that the hydroxyalkyl groups did not render such aminoazo compounds water-soluble. Nevertheless, later experience showed that such groups greatly facilitated the dispersion of azo compounds containing them as *N*-substituents with appropriate dispersing agents, the resulting dispersions having good affinity for acetate rayon. Still greater ease of dispersion and superior penetration of thick fabrics such as crêpes were obtained with dyes

patented by I.C.I. in which the hydroxyalkyl group was replaced by a polyethenoxy group (e.g.  $C_2H_4 \cdot [O \cdot C_2H_4]_n \cdot OH$ , where *n* is a small integer)<sup>11</sup>.

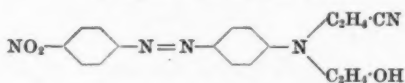
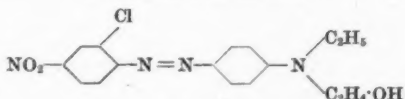
The constitutional features just referred to are well exemplified by the following further examples of commercial dyes—



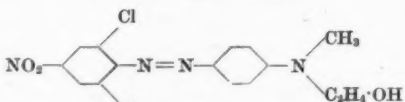
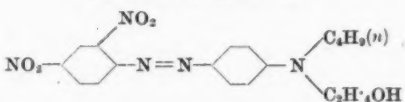
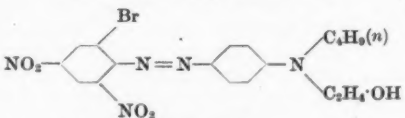
Dispersol Fast Orange A



Dispersol Fast Scarlet B

Celliton Fast Scarlet RN<sup>13</sup>

Dispersol Fast Crimson B

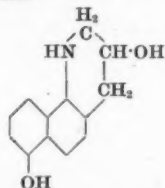
Celliton Fast Brown 3R<sup>13</sup>Celliton Discharge Violet 2R<sup>14</sup>Celliton Discharge Blue 3R<sup>15</sup>

The fact that by the use of 6-bromo- and 6-chloro-2:4-dinitroanilines as diazo components it was possible to obtain from benzenoid coupling components dischargeable monoazo blue dyes of reasonably good light fastness was discovered independently by I.G.<sup>16</sup> and I.C.I.<sup>17</sup>. Previously, monoazo blue dyes for acetate rayon had been obtained from other 2:4-dinitroanilines (e.g. 6-methyl, 6-methoxy, or 6-ethoxy derivatives) or even 2:4-dinitroaniline itself with  $\alpha$ -naphthylamine derivatives as coupling components<sup>17a</sup>. These had very poor light fastness. A later patent<sup>18</sup> by Geigy showed that if with diazotised 6-halogeno-2:4-dinitroanilines certain *N*-derivatives of *m*-aminoacetanilide were used, still greener blues could be obtained; in fact, blues, though redder, could be obtained with 2:4-dinitroaniline itself.

Investigations on the dispersed azo types during the last ten years or so, to judge from published

patents, have been mainly concerned with extending the range further into the blue (towards the green), and with achieving greater brightness and readier dispersibility. Much work has been done on new components, especially coupling components.

Before the recent war, I.G. had investigated the use of 2-aminobenzthiazoles as diazo components<sup>19</sup>. They tend to produce deep shades, and with *N*-hydroxyalkylated coupling components give very bright dyes, though these have only moderate light fastness. The 6-alkoxy-2-aminobenzthiazoles were found to be particularly valuable for their bathochromic effects. Celliton Discharge Pink BRF is one example of a commercial dye from this type of diazo component, its constitution being 6-methoxy-2-aminobenzthiazole → *NN*-bis-β-hydroxyethyl-aniline. By combining this type of diazo component with α-naphthylamine derivatives such as 1-β-hydroxyethylamino-5-naphthol (acid coupled) blue dyes were obtained. Dyes yielding still greener blues resulted from the use of the condensation product of 1:5-amino-naphthol and epichlorohydrin, the conditions of condensation being so chosen as to effect ring closure to give 3:1'-dihydroxy-7:8-benzo-1:2:3:4-tetrahydroquinoline—



Celliton Discharge Blue 5G was obtained by acid coupling of this component and diazotised 6-methoxy-2-aminobenzthiazole<sup>20</sup>. This type of reaction with epichlorohydrin can be applied also to primary and secondary amines of the benzene series<sup>21</sup>, the ring-closed tetrahydroquinoline derivatives in all cases giving much deeper colours than the corresponding open-chain hydroxypropyl compounds. A coupling component of this type is employed for Celliton Blue 2RF, which is 6-bromo-2:4-dinitroaniline → 3-hydroxy-7-methyl-1-sec.-butyl-1:2:3:4-tetrahydroquinoline<sup>22</sup>.

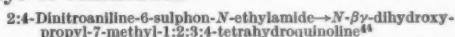
A serious fault arising with blue dyes for acetate rayon, particularly those of the anthraquinone series, has been their sensitivity to burnt coal-gas fumes. Exposure of dyed material to such fumes can result in considerable loss in depth of shade and often in change of hue as well. Work done at Leeds some years ago by Rowe and Chamberlain<sup>23</sup> showed that this effect was due to the presence of oxides of nitrogen in such gases. It should be noted, however, that there are common sources of oxides of nitrogen other than the combustion of coal gas, e.g. coal fires and electric fires, and exposure of acetate rayon dyed with these sensitive blue dyes in the vicinity of such sources can also result in this fading. A good deal of research has been done with the object of overcoming this defect either by synthesis of better dyes or by discovery of protective agents having affinity for the fibre which can react preferentially with the active constituents of such harmful atmospheres. Duranol

Inhibitor GF (ICI) is a product fulfilling the latter purpose.

A very large number of patents on azo dyes for acetate rayon have appeared during the last ten years or so by the Eastman Kodak Co. of America. This company appears to have entered this field of dyemaking activity later than most other manufacturers, and has marketed a range of dischargeable dyes known as Eastone colours. Many of their patents relate to dyes from coupling components containing a heterocyclic or hydroaromatic ring system. With particular diazo components they have used *N*-alkyl- or *N*-hydroxy-alkyl-tetrahydroquinolines and -benzquinolines of the types already referred to. In addition they have used—

- 2-Substituted 4:6-diketopyrimidines<sup>24</sup>
- 1-Aryl-5-imino- or 1-aryl-3:5-diketo-pyrazolidines<sup>25</sup>
- Sulphazones<sup>26</sup>
- Benzmorpholines<sup>27</sup>
- 4(*N*)-Phenyl-2-morpholones<sup>28</sup>
- Indoles<sup>29</sup>
- 6:7-Benzindoles<sup>30</sup>
- 2:3-Dihydroindoles<sup>31</sup>
- Tetrahydro-1:10- and -1:7-phenanthrolines<sup>32</sup>
- Octahydro-1:10- and -1:7-phenanthrolines<sup>33</sup>
- Tetrahydrofurfurylamines<sup>34</sup>
- N*-Nitroalkyl-arylamines<sup>35</sup>
- Tetronic and tetramic acids<sup>36</sup>
- 5- and 8-Aminoquinolines<sup>37</sup>
- 5:6:7:8-Tetrahydro-2:4-dihydroxyquinolines<sup>38</sup>
- Julolidines<sup>39</sup>
- 2-*N*-Alkyl-*N*-arylamino-4:6-diamino-1:3:5-triazines<sup>40</sup>
- Tetrahydrocinnolines<sup>41</sup>
- Lilolidines<sup>42</sup>
- Tetrahydroquinazolines<sup>43</sup>

Eastman Kodak draw special attention to a blue dye of constitution—



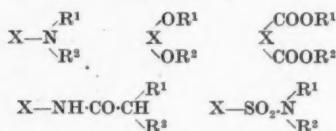
Dyes of this type and corresponding ones from benzmorpholines are said to give blue dyeings having good fastness to washing and light and good dischargeability, and to have very good affinity for the fibre at temperatures as low as 60–65°C. This type of blue dye has also been found to have quite good fastness to burnt gas fumes. Substitution at the 2 position of the tetrahydroquinoline derivative by methyl is said to improve speed of dyeing at lower temperatures, and to give violets and blues of good fastness to light and burnt gas fumes<sup>45</sup>.

4-Nitroaniline-2-sulphonamide derivatives have been widely used as diazo components by Eastman Kodak with a great variety of coupling components for acetate rayon dyes. In place of the 2-sulphamyl group that firm has also used -CO·Alk<sup>46</sup>, -SO<sub>2</sub>·Alk<sup>47</sup>, and -CO·O·Alk<sup>48</sup> groups and the fluorine atom<sup>49</sup>. The use of diazotised 4-nitroanilines carrying in position 2 an -SO<sub>2</sub>·CH<sub>3</sub> group with *N*-hydroxyalkyl-1:2:3:4-tetrahydroquinolines and benzmorpholines carrying a methyl group in the 2 position is also said to give dyes having excellent fastness to light and burnt gas fumes<sup>50</sup>. The trifluoromethyl group has also been used in place of methyl in a similar position as well as in many other components<sup>51</sup>, including trifluoroacetylated compounds<sup>52</sup>.

In connection with the colouring of cellulose acetate in the mass, prior to spinning, British Celanese Ltd. have patents in which they describe



azo compounds containing long-chain alkyl substituents. Thus it is said that the dye 2:6-dichloro-4-nitroaniline  $\rightarrow$  1:3:5-xenol, when *O*-methylated, reduced, then diazotised, and coupled to *m*-stearoylaminodiethylaniline, can be dissolved in a 25% solution of cellulose acetate in acetone and dry-spun to give a yarn dyed a full red which is very fast to wet scouring treatments<sup>53</sup>. Fast blues are similarly produced from the same coupling component if *p*-nitroaniline  $\rightarrow$  2:5-dimethoxyaniline is the diazotisable aminomonoazo compound<sup>54</sup>. Non-phototropic golden-yellow filaments of good fastness to scouring are obtained by use of the disazo compound aminoazobenzene  $\rightarrow$  oleylphenol<sup>55</sup>, whilst yellow to red colorations of spinning masses are obtained from certain azo compounds containing two univalent aliphatic radicals  $R^1$ ,  $R^2$  each containing at least eight carbon atoms united by  $-C-C-$  linkages<sup>56</sup>. Groupings by means of which such radicals may be introduced into an aryl dye nucleus  $X$  are exemplified by—



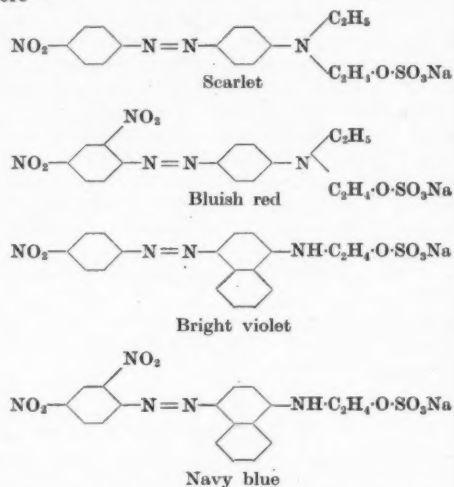
Dyes of these types are said to have little or no affinity for acetate rayon when applied in the ordinary way as aqueous dispersions. Their high solubility in organic liquids, especially acetone, facilitates the preparation of coloured spinning solutions. Fibres of exceptionally clear hues and free from "greasy" appearance are said to be obtained on spinning such solutions. The fastness to washing is said to be excellent. However, good solubility in acetone can be a drawback, since effect threads of acetate rayon in cotton goods may have to withstand Trubenising.

#### WATER-SOLUBLE DYES FOR ACETATE RAYON

One of the most important developments of recent years in connection with dyes for acetate rayon has been the search for and the production and marketing of water-soluble dyes capable of direct application to the fibre by methods similar to those employed with direct dyes for cotton and viscose. Such methods involve controlled exhaustion of the dyebath by addition of electrolytes such as sodium chloride or sulphate, and it would be the logical objective to colour acetate rayon by comparable methods of application. It would also avoid the troublesome extra manufacturing processes involved in preparing adequately dispersed and stable pastes and powders of the water-insoluble types, as well as difficulties for the dyer connected with reaggregation of such dyes on storage.

In 1920 Green and Saunders described a new type of acid dye, which they applied to wool and silk, by forming sulphuric esters of hydroxyalkyl derivatives of various types of dyes—azo, anthraquinone, amine, thiazine, triphenylmethane, etc.<sup>57</sup>. They called these "sulphato" dyes, and for the azo examples used as coupling components sulphated *N*-hydroxyalkylarylamines.

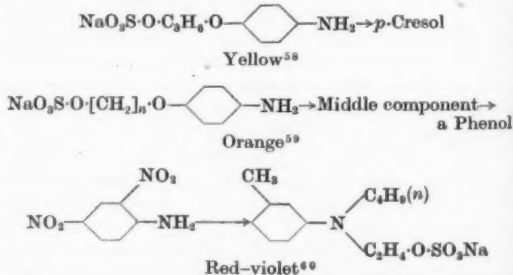
In a later patent<sup>57a</sup> it was stated that some of the dyes described by Green and Saunders, and certain other dyes, particularly those containing nitro groups, were suitable for dyeing acetate rayon. The colours of the dyes described ranged from yellow to orange, red, violet, and blue, the violets and blues being obtained from sulphated *N*- $\beta$ -hydroxyethyl- $\alpha$ -naphthylamine as coupling component. Examples recorded in the patent were—

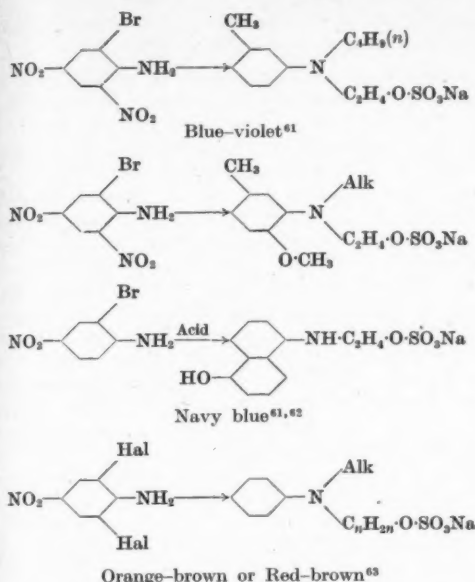


However, the violet and blue dyes had only poor light fastness; the yellows were phototropic, and the oranges either were phototropic or possessed inadequate light fastness or water solubility to compete with certain dispersed orange dyes, with the result that a very limited colour range of useful dyes could have then become available.

Work on this type of dye was resumed by I.C.I. about 1934, with the result that not only were violet and blue dyes having reasonably good affinity and light fastness obtained, but valuable light-fast yellow, orange, and brown dyes as well. The yellow and orange dyes were based on the use of sulphuric esters of aminophenyl hydroxyalkyl ethers as diazo components for certain monoazo and disazo combinations. The violets, browns, and, for the most part, the blues were obtained from *p*-nitroanilines as diazo components and benzenoid amino coupling components, all suitably substituted.

Examples from I.C.I.'s patents of that period which illustrate the way in which these colours were obtained are as follows—





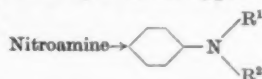
Azo dyes solubilised in this way have been marketed by I.C.I. under the trade name of Solacet dyes. They are water-soluble and dischargeable, and have excellent power of penetration, which makes them particularly suitable for dyeing heavy acetate rayon materials such as crêpes. Their rate of dyeing can be controlled at will by suitable addition of an electrolyte such as salt. This makes the matching of shades and the production of level mode shades much easier and more controllable than with the dispersed types, some of which tend to rush on to the fibre as the dyebath temperature approaches the ultimate dyeing temperature. They have superior washing fastness to the dispersed types. They are also suitable for printing acetate rayon.

Since 1941 further patents on dyes of this type have been taken out by I.C.I. Some of these relate to dyes which are said to have a higher affinity for acetate rayon than previously known water-soluble dyes of similar hue and constitution, with the result that they are particularly suitable for dyeing acetate rayon from long-liquor dyebaths such as are used in dyeing with the winch. They also have very good washing fastness properties, being somewhat superior to the Solacet dyes originally marketed. They follow the dyes of the earlier patents in broad constitutional pattern, their distinguishing chemical features being in the coupling components employed.

Thus, monoazo yellow dyes are obtained from diazotised sulphuric esters of aminophenyl hydroxyalkyl ethers and certain 2- or 3-hydroxydiphenylene oxides<sup>64</sup> or phenols corresponding to *p*-cresol but with the methyl group of the latter replaced by certain C<sub>2</sub>-C<sub>8</sub> hydrocarbon residues (alkyl, cycloalkyl, aralkyl, and aryl)<sup>65</sup>. Disazo orange dyes are obtained from similar first components, middle components of the benzene or naphthalene series, and *ortho*-substituted phenolic end components, the *ortho* substituent being a hydrocarbon radical of at

least four carbon atoms<sup>66</sup>. Reds, browns, violets, and blues are obtained with *p*-nitroaniline or certain halogeno, nitro, or cyano derivatives thereof as diazo components and, as coupling components, the sulphuric esters of *N*-hydroxyalkylanilines also having as *N*-substituents groups such as *n*-octyl,  $\beta$ -phenylethyl,  $\gamma$ -phenoxypropyl, and phenyl<sup>67</sup>.

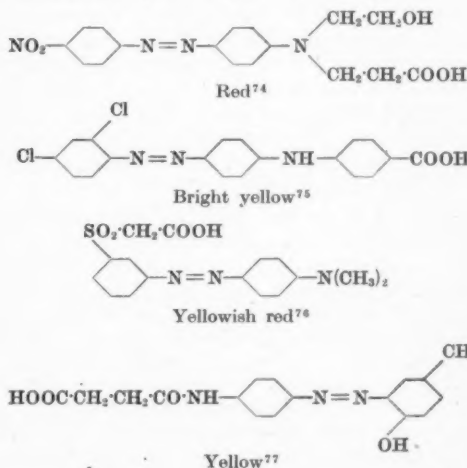
The replacement of the hydroxyalkyl sulphuric ester group R<sup>2</sup> in dyes of the type—



(R<sup>1</sup> = H, Alk, etc.) by a sulphoalkyl group (e.g. -CH<sub>2</sub>·CH<sub>2</sub>·SO<sub>3</sub>Na) also gives water-soluble dyes having affinity for acetate rayon<sup>68</sup>. Such dyes are formally related to the Ionamines, in which, as already mentioned, *N*-sulphomethyl is the solubilising group. Unlike the latter, however, the dyes in which the sulpho group is not attached to the  $\alpha$ -carbon atom (with respect to the amino nitrogen) do not split off this group during the dyeing operation, so that the hue of the dyeing corresponds to that of the dye originally put into the dyebath.

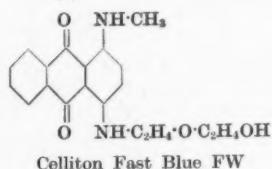
The patenting of sulphuric ester azo dyes and the marketing of the Solacet dyes by I.C.I. during the 1930s provoked considerable activity in the field of water-soluble dyes for acetate rayon on the part of other dye manufacturers. This is revealed by their patents and, as regards the I.G., by information collected by British and American investigating teams.

Phosphorous ester<sup>69</sup> and thiosulphuric ester<sup>70</sup> groups were employed in place of the sulphuric ester group by I.G. in some of their patents, but they led to inferior light fastness. Both S.C.I. (Basle)<sup>71</sup> and I.C.I.<sup>72</sup> have described soluble dyes obtained by monoesterifying certain dicarboxylic acids such as maleic, succinic, and phthalic acids with appropriate *N*-hydroxyalkylated amino-monoazo compounds, whilst the former firm have also used the sulphochloroacetic ester group for solubilising such compounds<sup>73</sup>. Dyes solubilised by carboxyl groups have also been described by I.G. in classes exemplified by the following—

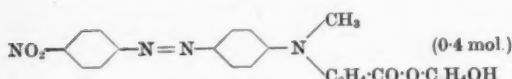
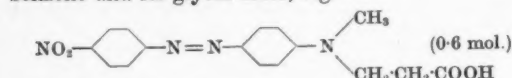


For dyes of the type exemplified by the first formula arylaminopropionic acids were used as coupling components; these were made available by addition of acrylic acid to arylamines.

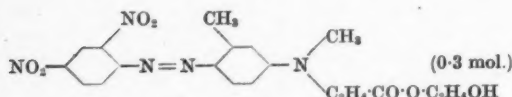
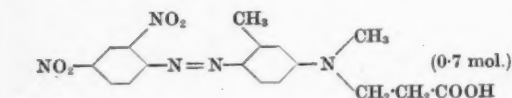
Before the recent war ended I.G. had developed a short range of six azo and one anthraquinone water-soluble dyes<sup>78</sup>. Their yellow was to be a product patented by I.C.I., of a type already described<sup>68</sup>. Their blue was an old commercial dye of theirs—



Each of the remaining five azo products consisted of a mixture of a 4-nitro-4'-carboxyalkylaminoazobenzene and its glycol ester, e.g.—



Acetate Silk Scarlet 5892



Acetate Silk Violet 5739

### Dyes for Nylon

Nylon is a generic term for fibres obtained from superpolyamides. More particularly it is applied to fibres from condensation products of adipic acid and hexamethylenediamine. Such fibres were first discovered and manufactured by Du Pont in America, and were later manufactured by British Nylon Spinners Ltd. in this country.

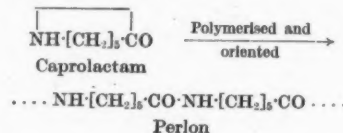
It was an early observation that the dispersed and water-soluble dyes used for the colouring of acetate rayon were very suitable for the colouring of nylon yarns and fabrics. Certain similarities in dyeing behaviour between nylon and wool or silk were revealed also, similarities which might reasonably be expected from similarities in chemical constitution. Provided they are selected with reasonable regard to measurements of dyeing rate and associated properties, dyes of the Duranolo (ICI) and Dispersol types offer the simplest prac-

tical method of effecting the coloration of nylon yarn and fabrics, particularly nylon hose.

However, for certain classes of goods, greater fastness properties may be required. For example, in woven and knitted fabrics, higher standards of light and washing fastness will be required than are obtainable with dispersed dyes. Other types of dyes, especially acid and direct dyes, may, and frequently do, surpass dispersed dyes in respect of range of colour and fastness properties but often fail to give satisfaction on the score of penetration, levelness, and compatibility. On the other hand, the high washing fastness associated with water-soluble dyes of the Solacet, acid, and direct classes on nylon materials is sufficient to meet all except the highest guaranteed standards. By selection from classes of soluble dyes it is possible to obtain a wide range of colorations of every hue with light fastness at least 5, and in many cases as high as 6, on the 1-8 scale. There are indications that, for a very limited range of hues, the Solochrome (ICI) dyes might give the desired exceptionally high standard of fastness for guaranteed work which is provided by vat and azoic types in the case of cellulosic fibres and silk.

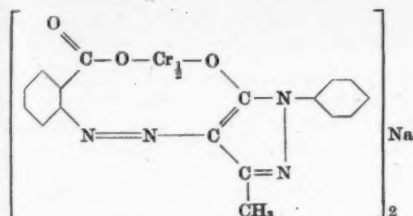
In view of what has just been said it is not surprising that the marketing of nylon goods has not been followed by a flood of patents for new dyes expressly for use with nylon, but the suitability for nylon of dispersed and Solacet classes of acetate rayon dyes is frequently reflected in the reference to the colouring of nylon in patents concerned primarily with dyes for acetate rayon.

In Germany, I.G. developed a rather different "nylon" from that made in America and this country. On cost considerations, I.G. selected the polymer from caprolactam for fibre development and called the fibre *Perlon*<sup>79</sup>—

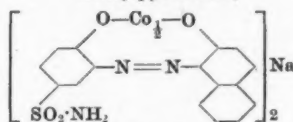


Whilst I.G. found that dyes commonly used for dyeing acetate rayon, their Celliton and Celliton Fast dyes, were most convenient for dyeing Perlon, giving good penetration, they developed a complete hue range of dyes especially for the latter which they called *Perlon Fast colours*. These were chiefly azo dyes, premetallised with chromium or cobalt, and previously produced in combination with certain organic bases for coloration of lacquers, plastics, etc. under the name *Zapon Fast colours*. A few unmetallised anthraquinone dyes were included, and an azomethine yellow. The premetallised azo dyes were stated to be water-soluble in the form of sodium salts, this solubility being due to metallisation with a metal salt: dye ratio such that a free valence of the metallic portion of the dye complex remains for salt formation. They were prepared in a physical condition particularly suitable for application to Perlon. Examples were—





Perlon Fast Yellow G  
(Chromium complex of anthranilic acid → phenyl-  
methylpyrazolone)



Perlon Fast Red 3BS  
(Cobalt complex of 2-aminophenol-4-sulphonamide →  
β-naphthol)

I.G. stated that, in general, the light fastness of these dyeings on Perlon is reasonably good and the wash fastness satisfactory. Their premetallised Palatine Fast wool dyes were discarded in favour of the Perlon Fast dyes as far as Perlon was concerned.

Finally, the author wishes to thank Messrs. Imperial Chemical Industries Ltd. (Dyestuffs Division) for permission to publish this paper.

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- E.K., *U.S.P.* 2,226,174.
- E.K., *U.S.P.* 2,196,757.
- E.K., *U.S.P.* 2,198,002.
- E.K., *U.S.P.* 2,221,020.
- E.K., *U.S.P.* 2,196,776.
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- E.K., *U.S.P.* 2,231,707.
- E.K., *U.S.P.* 2,342,678.
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#### Discussion

Prof. W. BRADLEY: Has the phototropic behaviour of some of the monoazo dyes referred to been related to *cis-trans* isomerisation of the form—



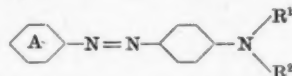
It seems that quite a number of those substituted *ortho* to the azo linkage will exist only as one stable form, and therefore may not show this property.

Basic dyes were important in the early days of acetate rayon dyeing, and I would like to know whether there have been any subsequent developments. I realise that they were usually unsatisfactory in respect of light fastness, but the introduction of quaternary ammonium groups appears to be feasible.

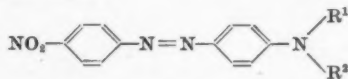
Mr. KNIGHT: The phototropic behaviour of certain aminoazobenzene derivatives has been related to *cis-trans* isomerisation by L. von Mechel and H. Stauffer (*Helv. Chim. Acta*, **24**, 151E-161E (1941); *J.S.D.C.*, **58**, 131 (1942)). This published work suggests that phototropy is not connected with any alteration in the electronic structure of the dye, i.e. conversion into a metastable condition,

but that conversion into the photomeric condition is more probably due to displacement of the actual dye molecule as in *cis-trans* isomerism. However, changes in the electronic structure of the dye cannot be ruled out as a possible mechanism.

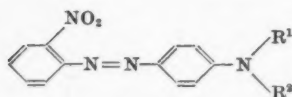
In a series of 4-aminoazobenzene dyes—



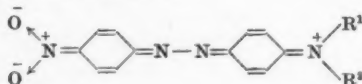
( $R^1$  and  $R^2$  = H, Alk, or  $\beta$ -hydroxyethyl) which we made about 1932, it was found that when the diazo component A contained a nitro group *ortho* or *para* to the azo linkage, or a nuclear acetyl group *para* to the azo linkage, the resultant dyes were invariably non-phototropic. When A contained no substituent or an *m*-nitro or *m*-acetyl group, or halogen, methyl, or methoxy in any position, or various combinations of these, it was found that the resultant dyes were invariably phototropic. We thought at the time that it was significant that in the former (non-phototropic) cases, quinonoid-type resonance structures involving the auxochrome could be written so as to show conjugation through the whole azo structure. Thus, with dyes of the general formulae—



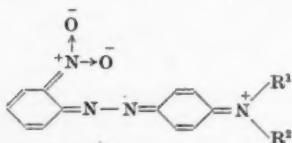
and



the resonance structures—



and

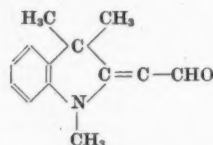


can be written respectively. No such resonance structure, involving a conjugated quinonoid system and taking in the auxochromic nitro group, can be written for the isomeric dyes from *m*-nitroaniline or for the compounds with halogen, methyl, or methoxy in any position in A of the above general formula. Hue relationships of any three isomeric mononitro compounds of the above types supported the quinonoid formulations for the *ortho* and *para* isomers, the *para*-nitrated compound being the reddest, the *meta* the yellowest, and the *ortho* intermediate between the other two (see also Reynolds, J.S.D.C., 60, 67 (1944), on the corresponding nitrophenylazophenols).

I cannot recollect having made any such dyes heavily substituted around the azo group which

did not also contain an *ortho*- or *para*-nitro group; these were non-phototropic.

With regard to basic dyes, the I.G. had developed, just before the war, a range of new printing colours for acetate rayon which they called Astrazone dyes. These had improved light fastness over the older type of triphenylmethane dyes originally used for dyeing. However, Astrazones are specifically for printing, as they have little affinity for the fibre from a dyebath. They are all derived from "Fischer's aldehyde" (1:3:3-trimethyl-2-methyleneindoline- $\omega$ -aldehyde)—



So far, they have not been marketed generally.

Some years ago we examined as acetate rayon dyes monoazo compounds containing a quaternary ammonium group attached to an *N*-alkyl substituent such as are described in B.P. 455,352 (I.G.). Such dyes, said to be water-soluble, had affinity for acetate rayon, but the water solubilities of those examples made were too low for practical use as such. Dyes of this type would also be incompatible with acid dyes such as the Solacets in the same bath, owing to mutual precipitation.

Dr. H. E. NÜRSTEN: What is the effect of the *N*-alkyl substitution of nitroaminoazobenzene dyes compared with that of the widely used *N*-hydroxyalkyl groups, taking Celliton Discharge Violet 2R as an example?

Mr. KNIGHT: Such dyes containing an *N*-ethyl group are usually somewhat bluer than corresponding dyes containing an *N*- $\beta$ -hydroxyethyl group, and those containing the *n*-propyl and *n*-butyl groups still bluer. Thus, Celliton Discharge Violet 2R (2:4-dinitroaniline  $\rightarrow$  *N*-*n*-butyl-*N*- $\beta$ -hydroxyethyl-*m*-toluidine) is a somewhat bluer violet than the dye from *N*-ethyl-*N*- $\beta$ -hydroxyethyl-*m*-toluidine, which in turn is bluer than that from *NN*-bis- $\beta$ -hydroxyethyl-*m*-toluidine. Such changes in substitution usually have little effect on light fastness.

Dr. C. B. STEVENS: Can the difference in hue of a given dye on nylon compared with the same dye on acetate rayon be related to the constitution of the dye in any way?

Mr. KNIGHT: Probably not. Generally speaking, insoluble reddish-violet, red, and reddish-orange acetate rayon dyes (Duransols and Dispersols) yield bluer and duller dyeings on nylon compared with those on acetate rayon; while yellows, bluish violets, blues, and greens yield dyeings of similar tone and brightness on both fibres. It is not immediately apparent that their hue relationships can be related to chemical constitution, especially as some of the dyes which give similar hues on both fibres belong to the azo class and some to the

anthraquinone class. Moreover, those which give dissimilar hues are also distributed between the same two classes.

Prof. W. BRADLEY: At one time it was held that a dye intended for dyeing acetate rayon could be successful only if its molecular size did not exceed a certain limit. Have later developments confirmed this requirement?

Mr. KNIGHT: This generalisation still holds to a considerable extent. The essential requirement is

the capacity of the fibre to dissolve the dye and so withdraw it from the aqueous phase. It is a common experience to find azo dyes of about the same molecular weight which differ markedly in their affinity for the fibre. Complexity of the dye structure as regards both number of azo groups and nature, number, and position of substituent groups can profoundly affect uptake of water-insoluble dyes by the fibre under identical conditions as regards dispersion and mode of dyeing.

## NORTHERN IRELAND AND SCOTTISH SECTIONS

Meetings held at the Queen's Hotel, Belfast, on 6th April 1949, Mr. J. H. JACKSON in the chair; and at St. Enoch's Hotel, Glasgow, on 12th April 1949, Mr. E. D. KENNEDY in the chair

### The Application of Colourless Fluorescent Dyes

E. C. CASPAR

The application of colourless fluorescent dyes has become of great importance during the past few years, since they enhance whiteness to a considerable degree. They are used in the textile, soap, paper, and laundry industries. It is possible that new fields of application will be found for these products. The process is called *white dyeing* or *optical bleaching*, the former term having been used for a long time in silk dyeing. The expressions *whitening agents* and *whitening effect* are also used. These fluorescing substances, mostly applied after the normal bleaching process, give a remarkable luminosity which could not previously be achieved, and which does not have any detrimental additional effect on the textile fibre.

A few papers have recently been published on colourless fluorescent dyes<sup>1</sup>, but it might be interesting to give a brief summary of the development of "white dyeing". It seems now to be generally agreed that the original idea of improving the whiteness of textiles was due to Kraus<sup>2</sup>, who attempted to use substances which give colourless solutions but have a strong fluorescence.

Kraus based his idea on previous investigations made by von Lagorio<sup>3</sup>, which had shown that fluorescent dyes reflect more visible light than they have absorbed from the visible part of the spectrum.

Fluorescence is an emission of light excited by radiation and lasting as long as the latter. Fluorescent substances therefore have the property of absorbing part of the light they receive and of emitting it at other wavelengths. In 1852 Stokes discovered empirically the following law: the exciting radiation is of shorter wavelength than the fluorescent light emitted. It can be explained by the higher energy of short-wavelength radiation, for only part of the energy absorbed is emitted as fluorescence. If the exciting radiation lies in the ultra-violet range and the fluorescent radiation in the visible, then an additional luminosity is obtained. This is the case, for instance, with basic dyes, such as Auramine O and Rhodamine B, and explains why this class of dyes possesses so good a brilliancy. Light from any source, especially diffuse daylight, contains a certain amount of

ultra-violet radiation, invisible to the human eye. If we dye a bleached fabric with a fluorescent substance which transforms ultra-violet rays into visible light, an additional luminosity is obtained. These substances must emit mainly blue or violet rays, which are complementary to the yellowness of the fibre, in order to produce a pure white. In other words, the use of fluorescing dyes gives the same effect as blueing, with the advantage, in contrast to the old method, that it does not result in a loss of light, but on the contrary in an increase in intensity in the visible spectrum.

Kraus made his first tests with aesculin, a glycoside extracted from the bark of the horse-chestnut tree. On half-bleached linen he obtained a similar effect to that obtained by full bleaching. But he was also the first to recognise the drawbacks of this substance, viz. insufficient affinity and deficient fastness to light. However, Kraus's idea was not forgotten. In 1934 Imperial Chemical Industries Ltd. made a patent application covering the use of derivatives of aminostilbenedisulphonic acid for the bleaching of cotton. These products were the first representatives of direct-dyeing fluorescing agents, after it had been recognised that both aesculin and the lithium salt of umbelliferone acetate, which had also been tried, were unsatisfactory because of their bad wet fastness and very bad light fastness. The development of suitable bleaching agents for the textile industry progressed rapidly, so that we now have a series of very good white-dyeing agents.

Although fluorescence is shown by a great number of organic compounds, the intensity of the fluorescence of a typical white-dyeing agent is always much stronger than that of its own colour; in other words, it does not show a substantial selective absorption in the visible spectrum.

Nearly all the technical products belong to the aromatic or heterocyclic series; many of them contain condensed ring systems.

On the evidence of the published literature, it appears that most of the whitening agents used on cellulosic fibres are derivatives of diaminostilbenedisulphonic acid. These are also used as additions to detergents and rinsing products. Benzimidazole



and glyoxaline derivatives are also advocated. Diphenylglyoxalonesulphonic acid is known especially for application to wool. It is not understood why an organic substance is fluorescent and what the determining factor in its formula is, but conjugated double linkages seem to have some importance.

In discussing the applications and properties of these colourless fluorescing agents, the term *whitening agents* will be used instead of "fluorescent substances". The effect obtained will then be called *whitening effect*. Both "optical bleaching" and "fluorescent bleaching" seem to be somewhat misleading, since the effect of whitening agents depends very much on the cleanness of the fabric to which they are applied. With dark or yellow material a *chemical bleaching* is essential. Whitening agents have no bleaching properties of their own in the ordinary sense. Because of their blue to violet emission they are much more similar to the bluing dyes used in tinting. The only difference is that they confer an additional luminosity on the textile. The expression *white dyeing* is, therefore, more logical.

The field of technical application of white-dyeing agents includes the textile, paper, detergents (both soap and synthetics), and laundry industries. Little is known with reference to pigments, lacquers, rubber, and plastics, but it is possible that some day a whitening agent will be found suitable for these products.

In the textile industry, whitening agents have had a very great success in the bleaching of white goods, especially of cotton. It became possible for the first time to obtain a degree and a quality of white that had been impossible before without greatly impairing the quality of the fabric. This is the great advantage of whitening agents. However, one cannot completely dispense with chemical bleaching. If the fabric is not already bleached, i.e. if it has not a sufficient degree of whiteness, then a colourless whitening agent with blue fluorescence cannot compensate for the yellow or brown colour of the fabric. Unpleasant colorations occur because the insufficiently bleached cellulosic fibre quickly becomes yellow under the influence of light and storage. Whitening agents do not cover up a change in the colour of the substrate.

Of course, there exist cotton goods that can be white-dyed very easily without any bleaching or at most with one single cleaning operation, notably cheap napped qualities for lining purposes, shoe linings, etc. It is also possible to avoid bleaching in the case of viscose rayons and staple fibres, but it is not then possible to obtain a pure, dazzling white.

In the treatment of multicoloured piece goods, the use of white-dyeing agents has proved very economic, because their application permits grey or scoured instead of bleached yarns to be used. The piece can be treated with whitening agents during finishing, with a very pleasant resulting effect. Cotton wadding can be made much whiter by the use of whitening agents. After the kier boiling and bleaching, the cotton can be treated during the rinsing operation. Successful tests have also

been made by adding specially resistant products to the boil-off liquor. The combed cotton sliver can be white-dyed during the bleaching process, e.g. with hydrogen peroxide, or during the rinsing.

Yarns can be white-dyed in bleaching or dyeing machines.

White-dyeing agents are especially recommended for the treatment of cotton knitted goods made of grey yarns, which are boiled off in the piece. The bleaching time can be substantially shortened by performing only one bleach with chlorine, followed by white dyeing, instead of a combined chlorine-hydrogen peroxide bleach.

In the manufacture of viscose rayon and viscose staple fibre (spun viscose), suitable white-dyeing agents have afforded new possibilities. The product can be added directly to the xanthate (viscose) before the spinning process, when the viscose rayon is brightened in the mass. Of course, it is necessary to have a product that is stable to the high alkali concentration and that will withstand the subsequent desulphurising and cleaning operation. This process is particularly interesting for viscose rayon dyed in the dope (spun-dyed), especially in light shades. Baby pinks, baby blues, and salmons obtained by the addition of the white-dyeing agent look brighter and purer. Blacks and navies become bloomier. Cotton, linen, and viscose piece goods are preferably treated in the finishing process on the padding mangle. Brightening and bluing can be carried out in one operation on the padding mangle by adding the products to the finishing liquors. Rayon crêpes are often treated on the winch in one operation in the hydrogen peroxide bleaching bath or by separate treatment.

It should be possible to add white-dyeing agents to peroxide liquors when working with continuous bleaching processes in J-boxes. Since these articles must usually go through the padding mangle, the white dyeing is best carried out at that stage.

Ribbons, bands, elastic bands, etc. are treated by dipping.

There are limitations to these white-dyeing processes with colourless fluorescent dyes. In the treatment of yarns, fine and glossy fibres need less dye than coarse and dull ones. If the percentage is too high, glossy material becomes immediately iridescent, i.e. the appearance of the textile changes with the direction of viewing and it shows a dichroic effect. Because of their optical properties, these whitening agents accentuate the defects of badly performed bleaching and non-homogeneous fibres. This is particularly noticeable in linen and hemp. It is much easier to brighten up a very fine linen batiste, which contains a lower percentage of non-cellulosic material, than heavy linen clothing containing relatively more impurities. Jute is particularly difficult in this respect.

White-dyeing agents, unfortunately, also show creases and chafe marks which would not be so evident had they not been treated.

Whitening agents can be used not only in the bleaching, i.e. in the finishing, of grey goods, but also in the dyehouse, in the printshop, and in the finishing of multicoloured woven goods.

In the dyeing of pastel colours, remarkably clear dyeings are obtained. The whitening agents should be added to the exhausted dyebath; a better effect is thus obtained than if the normal dye is applied to a previously white-dyed material.

The use of whitening agents to obtain clear white effects on multicoloured woven articles also has the advantage of brightening up the colours by contrast.

It is most important to note that the use of white-dyeing agents shifts the shades towards the blue, and this fact must be taken into account in dyeing baby pinks and salmons.

In calico printing, white-dyeing agents are used to brighten up white discharge patterns and for the amelioration of the contrast of coloured prints, either by a preliminary treatment or in a separate bath following printing and rinsing. Multicoloured discharge styles and direct prints show a brighter appearance, especially blues, greens, and greys. Provided the agent is stable to hydrosulphite, it may also be applied direct in the discharge paste. However, the addition of a whitening agent will not improve the dischargeability of a badly dischargeable dye: if a dye is not easy to discharge, the effect cannot be overcome simply by adding a white-dyeing agent.

In the wool trade, white-dyeing agents have not yet conquered the market, for there have been very few products suitable for application to wool. Then also white wool articles are not so frequent as white cellulosic textiles. However, whitening agents provide a cheap and easy means of obtaining white wool without damaging the fibre, which was impossible by the ordinary bleaching methods.

It is possible to obtain very pure whites on peroxide-bleached wool, by treating with products which are absorbed by the fibre from acid baths. These whites are far brighter than those obtained by bleaching with peroxide, hydrosulphites, bisulphites, or gaseous sulphur dioxide. Light fastness and colour have a determining influence on the possibilities of application of such a product.

The traditional shade of bluing agents used on cottons has not met with much success on wool, because one is not used to seeing bluish, chalky whites on this material. Milky, greenish shades are accepted for wool, and colder ones for cotton. As a consequence, whitening agents for wool should give a greenish fluorescence, which, combined with the natural hue of wool, will give a warm impression. The fastness to light of such products should be very good, because wool itself quickly turns yellow under the influence of light. The object of the treatment would certainly not be attained if the treated fabric appeared yellower after exposure to light than the untreated one.

White dyes can be used in the finishing of wool, especially in the dyeing of pastel shades, mainly baby pinks and blues on knit goods. The products are added to the dyebath, but they can also be used as an aftertreatment of the dyed fibre. There are great possibilities in the knit-goods trade, either on yarn or on piece goods, and also in the wool-felt industry for ladies' hats.

Silk can be white-dyed with the agents employed for wool as well as with those used for cellulose. Because of its natural gloss, silk has a very strong tendency to fluorescence and consequently to give fluorescent dyeings. It is therefore necessary to watch very carefully the amount of white-dyeing agent used. Exceptional difficulties are encountered in treating coarse silks, particularly tussore.

Up till now no satisfactory white-dyeing agent has been found for acetate rayon. It is true that weak effects can be produced, especially with acid dyeing, but the fastness properties are inadequate.

Among synthetic fibres, it is possible to white-dye nylon, which is comparatively difficult to bleach a pure white, simply by using the typical white-dyeing agents for wool.

In the paper industry the treatment of cellulose fibres is by far the most important application. However, for banknote paper, paper for securities, etc. it is possible to apply white-dyeing agents to wool mottling fibres. The process is fundamentally the same as for dyeing: the agents are applied in the beater. Finished paper can be treated either by a dip-dyeing process or by a coating procedure, employing the usual fillers and pigments. The white-dyeing agents used for this must be very stable to acid to withstand the precipitation of the rosin-size and alum without becoming yellowish. White-dyeing agents are used in the paper industry mainly for fine papers, cigarette papers, cellulose wadding, and crepe papers. Furthermore, they are usually combined with tinting dyes for use in the paper industry, since the most usual products almost always give too reddish an effect.

White-dyeing agents can be used in the soap industry for the following purposes—

(a) As additives to soap powders, being absorbed by and bleaching the textile during washing.

(b) Whitening of the soap or soap powder itself, so as to improve its appearance.

(c) A combination of (a) and (b).

(d) As additives to rinsing agents.

The addition of white-dyeing agents to washing agents of all kinds (soaps and synthetics) for the purpose of enhancing the whiteness of the textiles washed therewith has often been mentioned in patent literature. It is clear that this process will become very important in the future. Of particular interest in this connection are those products which simultaneously enhance the whiteness of the washing agent, an important sales point. Thus, in certain circumstances, an optical bleaching agent for soaps or powder washing agents can be of considerable commercial interest, although without action on the goods washed.

The addition of white-dyeing agents to rinsing agents, with consequent improvement of the appearance of the wash, is comparatively easily achieved, since it is merely a modification of the white-dyeing process, involving substantive absorption of the agent by the fibre. When these agents are combined with washing and rinsing agents for domestic use and for textiles, there is a certain danger of their accumulating on frequent washing.

If white-dyeing agents which are very fast to washing are employed, the concentration on the fibre will increase at each wash. Under certain conditions this may lead to the appearance of displeasing dyeing effects. Thus the products to be aimed at should be themselves very faint in colour and should not be too fast to washing. Furthermore, any decomposition products resulting from the action of light or boiling alkalis used in washing should also be colourless.

It is probable that at present no product exists which completely fulfils these desiderata. None the less, there are already some reasonably satisfactory products on the market.

In the laundering trade, rinsing agents containing white-dyeing agents are already in use. It is natural that peculiarities due to the optical nature of the effect should arise in this application. The varying degree of bleaching and of wear and incrustation with lime soaps and hydro- or oxy-celluloses of the textiles being washed gives rise to varying absorptive power for the white-dyeing agents. This may occasionally bring about too strong or too weak an effect with some articles. By combination with normal bluing dyes it is always possible to compensate for these variations to some extent.

For the sake of completeness the use of colourless fluorescent dyes as marking inks may also be mentioned. My own experiments have convinced me that such fluorescent marking inks may be used even with white-dyed textiles, since pronounced differences in the intensity of fluorescence and in the shade of the dyeing are visible under the ultra-violet lamp.

For use with cellulosic materials, a white-dyeing agent should be absorbed substantively by the fibre from aqueous solution, and also, when possible, by the padding method, so as to give a shade satisfying the traditional tastes, i.e. a greenish to blue tint. The wet-fastness properties should be as good as possible in order to guarantee the permanence of the effect. A white-dyeing agent should be stable towards weak acids and alkalis and should be compatible with other finishing agents. Whenever possible, it should be suitable for direct use in the bleaching vats. It should be stable to heat and to storage and should be as fast to light as possible. Consideration of these points alone makes it evident that a white bleaching agent, chemically considered, must be a very resistant product, all the more so when it is remembered that the quantities used can vary from only a few hundredths to a few tenths of one per cent.

Research is constantly in progress in an effort to find new products which will have better properties, particularly as regards shade and fastness to light. None the less, cleanness and the shade obtained play a decisive rôle in evaluation.

There is no absolute white. It will always remain a matter of taste to decide whether a certain brightening effect will produce a neutral white or whether brighter effects will not be given by faint green, blue, or red toning. White-dyeing agents depend for their emission on the ultra-violet

content of daylight, so that the effect can vary in strength and shade.

Since the ability of the human eye to differentiate between colours is greatly dependent on the intensity of illumination, it would appear that judgment of a white produced by the use of a fluorescent dye is frequently influenced by optical fatigue.

By using a fluorescence photometer, e.g. to measure the strength of fluorescence in solution and on material, an attempt can be made to eliminate the subjective factor. However, it is difficult to correlate the numerical values thus obtained with the visual effects of the resulting white. While it is comparatively simple to measure heat and electricity there are great difficulties in measuring light. These difficulties arise from the fact that heat and electricity are present even if mankind is absent, whereas there can be no light without the eye; without it there would be only electromagnetic waves.

The visual strength is also dependent on the shade. Here the conditions are similar to those applying to dyes. Just as it is impossible satisfactorily to compare numerically a blue and a red, so is it equally impossible to express the relative strength of a reddish and a bluish white-dyeing agent by a number.

The value of a white-dyeing agent, moreover, depends not only on its economy in use; the shade and fastness properties and possible applications are at least equally important.

The shade and fastness properties depend on the following factors—nature of the fibre, concentration, time, temperature, liquor ratio, pH, presence of additives, solubility, influence of light while in solution, whiteness and surface composition of the substrate, and illumination of the dyeing. A particularly interesting observation is that the colour of the fluorescence may vary with changes in concentration. With increasing concentration a displacement of shade is observed with many of the commercial products. Thus dyeings produced with the reddish products tend more towards yellow. At very high concentrations this gives a measure of the maximum brightening effect attainable with any given white-dyeing agent.

In the case of textiles which have been well prebleached, the maximum brightening obtainable does not play any great part. However, it is of importance with paper and soap and in other cases where a relatively dark material is to be brightened, and in finishing processes which impair the white effect (e.g. anti-crease finishing).

The maximum brightening must be regarded, in addition to the usual strength comparison at low concentrations, as a separate basis for evaluation. It gives a measure of the absolute effect and probably makes possible the detection of the degree of impurity present in products of similar chemical constitution.

The above also explains why no generally valid strength ratios can be given for two different brightening agents.

With all products the fastness to light in solution is inferior to that when the product is fixed on the



fibre. Thus, we have found that some of the best known strongly reddish products give solutions that, when exposed to diffuse daylight, lose more than half their intensity within an hour. This is not such a disadvantage in practice as might be thought, however, since the dye liquors are not exposed to light, but it should be taken into account.

The illumination of the dyed fabrics is also very important for the correct estimation of the whitening effect, because the slightest reflection of coloured light influences the judgment. Similarly, results will be different according as the object is observed during bright or cloudy weather. A disturbing factor still more important is the presence of snow on the ground illuminated by sunshine: under such conditions it is most difficult to make a correct evaluation.

Another difficulty in the comparison is caused by the difference in constitution of the various products. All the white-dyeing agents lose much of their intensity under artificial light because it contains very little ultra-violet radiation. Modern fluorescent lighting seems to give the best effect. The admixture of pure bluing dyes to whitening agents generally improves the shade of white dye under artificial light; however, it always affects the purity of the bleach.

The above remarks about shade, strength, and influence of light source apply also to the typical whitening agents for wool. It is, of course, important not to give a reddish shade to wool, because this would look unnatural; some substantive fluorescent whitening agents which also have affinity for wool show this clearly.

The typical whitening agents for wool can be used on bleached material in an acid bath. It is interesting to examine the affinity and the rate of exhaustion in a neutral bath, for it seems that in a neutral bath the affinity of bleached wool depends on its previous treatment. The wool will take up the dye only if it has previously been subjected to an acid treatment. It is therefore possible to obtain good whitening effects in a neutral bath only on condition that it has first

undergone an acid rinse. The difference between such wool and wool which has undergone an alkaline or neutral treatment still remains even after numerous rinses in distilled water after the acid treatment.

It would be also interesting and useful to have products which could be used in neutral or slightly alkaline baths. This would enable us to obtain good whitening effects on raw wool or fairly light-coloured wool by treating it either in a scouring operation or in a peroxide bleaching bath.

The light fastness of whitening agents for wool is of very great importance, because wool is very susceptible to yellowing.

Now, if we examine the light fastness of unbleached material, we see that the wool first becomes brighter under the influence of light, even without any whitening agent. This is probably the reason why some white-dyed samples which have been exposed to light for a short period (e.g. for 2 hr. in the Fadeometer) become brighter than the original unexposed samples. Of course, if the exposure to light is prolonged, the white effect diminishes. This is true of all products. When the fastness to light of the fluorescent dye is not particularly good, its decomposition products mask the original bleaching effect very quickly. If the exposure to light is continued for a longer period, the wool will acquire an unpleasant yellow or brownish shade. Should the decomposition products be coloured, then the treated samples will look darker than the untreated control samples.

The comparison of various strengths is much easier with products of similar shades than with whitening agents differing in constitution and hues. As the strength depends on both the temperature of application and the pH, it is possible to compare different samples only if their method of application is known.

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### MIDLANDS SECTION

Meeting held at the College of Technology, Leicester, on 15th September 1949, Mr. W. L. LANGTON in the chair

## Theoretical and Practical Aspects of Fluorescence, Luminescence, and Phosphorescence

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#### INTRODUCTION

Luminescence is quite an old subject, with a reliable history of some 350 years, and an extremely unreliable tradition extending to thousands of years, but it is only comparatively recently that it has found practical application in the textile industry. The scope of this application is still rapidly extending, and the part of this lecture which concerns textile applications must be regarded merely as an interim report.

#### DEFINITIONS

In order to make clear the scope of this subject, I propose to start by defining the phenomena concerned. Firstly, *luminescence*. This is a general term which covers any emission of light by a material, other than thermal emission. Any material which does not decompose if sufficiently heated emits light, the amount increasing with the temperature, becoming gradually red hot and then white hot. This is thermal emission of light

or *incandescence*. The maximum amount of light produced by thermal emission is fixed by the temperature, and is the amount produced by a so called "black body" at that temperature. At high temperatures, most solid materials approximate closely to black-body emitters. The essential feature of luminescence is that the material emits *more* light than a black body at the same temperature. In most of the practical applications of luminescence, the material is at normal temperature, at which there is, of course, no thermal emission of light, and the luminescent emission is aptly described as "cold light". However, in special cases, a heated material may produce luminescent and thermal emission simultaneously, and it is necessary to define luminescence in this way.

Now luminescence may arise from various causes. Light is a form of energy, and any material which emits light must previously have obtained the energy from somewhere. It may have come from chemical reaction, mechanical stress, bombardment by electrons or atomic particles, or by exposure to light. It will be convenient to take a rather free definition of "light" to include not only the visible range of wavelengths but those which are too short to be visible, the ultra-violet. Luminescence from this cause is called *photoluminescence*.

It must be emphasised that photoluminescence does *not* include simple reflection or scattering of the light, but implies a definite change in the wavelength of the light. The original light may include a wide range of wavelengths and the photoluminescence may overlap this range, but at any rate one can say that, if photoluminescence is present, there will be more of some particular wavelength emitted by the material than was present in the original light. The remaining phenomena to be defined—fluorescence and phosphorescence—are subdivisions of photoluminescence. *Fluorescence* ceases as soon as the exciting light is removed, while *phosphorescence* continues for an appreciable period afterwards. These definitions serve very well for practical purposes but are not entirely watertight from the theoretical point of view. The true difference between fluorescence and phosphorescence is found in the atomic processes by which they are produced, which will be mentioned later.

#### HISTORY

Having defined the phenomena to be discussed, we will now pass to a brief account of their history. The legends and fables of the Near and Far East are full of references to precious stones which shone in the dark, but these claims are not substantiated by our present knowledge. Some diamonds and certain types of fluorite show a short afterglow if they are rapidly transferred from bright sunshine to a dark room, but this is not the effect described by the legends, which speak of phosphorescence lasting for hours or days. Furthermore, diamonds are never mentioned in the legends, the stones generally being described as "carbuncles", the usual synonym for ruby, spinel, or garnet, none of which is phosphorescent. We can only say that

we have no evidence in support of these legends, while recognising that many other seemingly impossible legends have been found to have a basis of fact.

One other class of luminescence—*bioluminescence*, i.e. the production of light by chemical changes in living organisms—was certainly known in ancient times. Glow-worms and "sea-fire" must have been known from very early times; they are described by Aristotle, as also is the luminescence of rotting wood. References to phosphorescent jewels continue in the folk-lore of the Middle Ages, again without substantiation, but the established history of luminescence begins about the year 1600, when one Vincencio Casciarola heated certain stones in a furnace in the hope of extracting gold from them, and found instead that the calcined product emitted a reddish phosphorescence. This discovery led to much further experimental work, the products being known by many picturesque names, until eventually the term *phosphor* was generally accepted. The recipes for the preparation of these inorganic phosphors were entirely empirical and the products extremely variable, as until about fifty years ago it was not realised that the phosphorescence was dependent upon the presence of small proportions of particular impurities. This was not established until Verneuil and Lenard carried out research using pure materials.

Fluorescence of aqueous solutions was observed somewhat earlier than phosphorescence, but for some 300 years it was merely regarded as a special kind of dispersion or diffusion of the incident light, and it was not until 1852 that Stokes proved that the wavelength of the emitted light was always longer than that of the incident light, a generalisation now known as Stokes' law.

In the 1870s, Goldstein and Crookes began, independently, investigations on luminescence produced by cathode rays, which are fast-moving electrons produced by an electric field in an evacuated tube.

Although luminescent phenomena were of great scientific importance, until recently they found little practical application. Apart from luminous paints for watch-dials, luminescence was mainly regarded as a curiosity.

#### THEORY

At this point it is desirable to give some explanation of the origin of luminescence, and the difference between fluorescence and phosphorescence, in order that the limitations to practical application may be understood. In the absence of this theoretical explanation, the user of fluorescent products may be puzzled, for instance, as to why the chemist simply cannot supply a colourless product having a red fluorescence.

The emission of light is caused by changes in the energy levels of atoms; the wavelength varies inversely with the energy. For single atoms, the number of energy levels, and hence of wavelengths, is comparatively small; for molecules it is much greater, and for molecules in the solid state, interaction between adjacent molecules increases the number of levels to the point where the spectrum is practically continuous.



Before an atom or molecule can emit light, its energy level must first be raised by an outside agency, which may be thermal, chemical, mechanical, or the impact of an electron or atomic particle, or of light. This last source is the one which is of most interest to us. Since the energy supplied must be greater or equal to that emitted, it follows that the wavelength of the exciting light must be shorter than or equal to that emitted, a fact discovered by Stokes long before the structure of the atom was known. The excess of energy supplied over that re-emitted is absorbed by motion of the atom or molecule, and appears as heat.

Stokes' law is of great technical importance for the following reason. Any substance which is coloured absorbs light, regardless of whether it is fluorescent; many dyes are not fluorescent. We may note in passing that if the absorbed energy is not re-emitted as light, it generally reappears as heat or chemical change. However, considering a fluorescent dye such as Rhodamine, its fluorescence is orange, and Stokes' law suggests that it should absorb green light; in fact it does so, reflecting red and blue, and hence has a magenta colour. On the other hand, a colourless substance can absorb no visible light, and its absorption, if any, must be in the ultra-violet. Its fluorescence will probably be violet or blue, and this is found to be generally the case. Fortunately, "optical bleaches" are required to fluoresce blue, as they must necessarily be colourless. Only a few colourless substances having green or red fluorescence are known, and the emission is weak and of no technical importance.

The essential difference between fluorescence and phosphorescence lies in the manner of re-emission of the energy. In both processes, the energy is absorbed by one electron in an atom. In fluorescence, the electron immediately falls back to a much lower level (not necessarily its normal state), re-emitting the energy as light. In phosphorescence, the electron falls back to an intermediate level slightly below the higher one. From here it may be unable to return to the normal level, for reasons which we cannot go into here but which are explained by quantum mechanics. It therefore must remain in the intermediate level until it acquires sufficient energy—generally from thermal agitation—to raise it to the higher level, from which it again has a chance to fall to the normal level, with emission of light. The average time which the electron takes to acquire this energy determines the duration of phosphorescence, and may be anything from a small fraction of a second to many hours.

In practical examples both of fluorescent and of phosphorescent materials, more than one substance may be present, and the system of energy levels, and hence the light emitted, depend entirely on the substances present. For example, an organic substance may show no fluorescence in the solid state, strong fluorescence in one solvent, and little or no fluorescence in another. The presence of small amounts of particular impurities may greatly affect the fluorescence. It is impossible to generalise

about such causes of loss of fluorescence, but there are two main causes which must be briefly mentioned. The first, which applies to liquids and solutions, is due to the fact that, although the time during which an atom or molecule is at the higher energy level is very short, less than a millionth of a second, there is nevertheless a chance that during this time it will collide with another molecule and lose part of its energy, and hence be unable to re-emit it as light. This chance obviously increases with the concentration. The second cause is that, whereas dilute solutions consist of single molecules, in stronger solutions the molecules become aggregated into groups of as many as fifty, and the energy levels for such an aggregate may differ considerably from those of a single molecule. In practice, aggregation generally leads to a great reduction in fluorescence. Owing to both these causes, therefore, the fluorescence does not increase steadily with concentration, but reaches a maximum and then decreases. In solids, collisions cannot occur, and so far as we can generalise at all, we can only say that loss of fluorescence is due to disturbance of the system of energy levels by impurities.

#### LIGHT SOURCES

The quality of the illumination used to excite fluorescence and phosphorescence is of paramount importance; for instance, where "optical bleaches" are employed, it is obviously useless to expect them to be effective when there is no ultra-violet in the illumination, but this point tends to be easily overlooked.

Sunlight contains a small proportion of ultra-violet radiation in the region immediately adjacent to the violet end of the spectrum, i.e. at wavelengths of 3000–4000 Å. Shorter wavelengths are present in the light leaving the sun, but are mostly absorbed in the earth's atmosphere.

Electric lamps of the ordinary incandescent filament type produce considerably less ultra-violet than sunlight. The amount may be increased by over-running the bulb, as is done with the Photoflood and Nitraphot bulbs used for photography; the life of the bulb is greatly reduced, of course. Bulbs of this type are used in America as ultra-violet sources, but are not very popular in this country.

The principal artificial source of ultra-violet radiation is the electric discharge tube, in which the passage of an electric discharge through mercury vapour produces light of a range of separate wavelengths, in both the visible and ultra-violet, a type of luminescence already mentioned. Discharge tubes fall into two classes—(i) the low-pressure or so-called "cold" quartz lamp, the light from which consists almost entirely of one wavelength, 2537 Å.; and (ii) the high-pressure type, much of the light of which consists of the group of lines around 3660 Å. with small proportions of several other lines.

The modern "daylight" fluorescent tubes used for interior illumination are examples of discharge tubes, but the ultra-violet is almost entirely converted into visible light by the coating of a mixture of inorganic fluorescent materials on the inside of

the tube. A small percentage of ultra-violet penetrates the coating, so that "optical bleaches" are effective under this illumination.

All the aforementioned sources produce visible as well as ultra-violet radiation, and when the latter alone is required, as is often the case for researches on fluorescence, the visible light must be removed. This is normally done with a filter of Wood's glass, which contains nickel oxide and appears almost black to the eye, but which passes a wide band of the ultra-violet just below the visible violet.

#### NON-TEXTILE APPLICATIONS

The applications of luminescence outside the textile industry are of a very varied character. Fluorescence naturally finds many applications in the identification, analysis, and testing for purity of materials, but as already mentioned, fluorescence is very sensitive to the presence of impurities, and any particular industrial problem has, therefore, to be treated on its own merits; it is quite impossible to generalise. In many cases, fluorescence examination has been found valuable, particularly where the examination is always carried out by the same observer, as small differences in the quality of fluorescence may be seen which are difficult to describe in words. In other cases, where more than one impurity which affects the fluorescence is present, fluorescent examination is useless and the results may be misleading.

Fluorescence is also widely used for the prevention of imitation or forgery of a product. Its value for this purpose is very limited, however, since by this time most imitators are well aware of the existence of fluorescence, and take care to make the necessary additions.

The fluorescence of solutions finds several applications. During the war, the position of aircraft forced down on the sea was indicated by fluorescent dye spreading over the surface of the water. Solutions of fluorescein have been used to trace the course of underground rivers and to indicate leaks in water mains. The time of circulation of solutions in a large industrial plant may also be measured. The same principle is applied on a small scale to measure the time of circulation of blood in the human body. Fluorescein was used to indicate leaks in the "Pluto" pipeline. In recent research on the common cold, fluorescent substances introduced into the nostrils have been shown to distribute themselves over one's surroundings with amazing rapidity.

Luminescent paints are one of the oldest applications of luminescence. They fall into three classes—fluorescent, phosphorescent, and self-luminous.

Fluorescent paints require to be illuminated by an external source of ultra-violet radiation, but their luminosity ceases as soon as the source is switched off, which is an advantage for some purposes. They were used to some extent for rendering objects visible during blackouts in the recent war, and are apparently widely used in the interiors of theatres and cinemas in America for

indicating the positions of gangways and seats, but I have not heard of their use for this purpose in this country. The fluorescent constituents may be either organic or inorganic; the latter are less brilliant but much more permanent, particularly where the paint is liable to exposure to daylight.

Phosphorescent paints require exposure to light before they become luminous, but then remain so for several hours. Exposure to daylight is not necessary; a good commercial paint is activated by a minute's exposure to a bright electric light. These paints were also used during the war to render objects visible in the blackout. They are composed of mixtures of inorganic phosphors, but the exact details are kept secret by the manufacturers. The practice of German firms has been reported by Allied investigators<sup>1</sup>.

Self-luminous paints are also composed of inorganic phosphors, but contain in addition their own source of energy for excitation of the phosphor. It has already been mentioned that excitation is produced by bombardment with electrons or atomic particles. A steady and self-contained source of these is provided by a radioactive substance. Radium itself is not generally used, on account of cost; the usual substance is mesothorium, which emits an electron and forms radiothorium, which in turn emits an  $\alpha$ -particle (the nucleus of a helium atom).  $\alpha$ -Particles are particularly effective for the excitation of luminescence. Mesothorium provides an adequate source of excitation for upwards of ten years, but the life of the paint is actually limited rather by the destruction of the phosphor itself by the  $\alpha$ -particle bombardment.

These paints are mainly used for figures on the dials of watches and instruments. Their application is limited by the high cost and shortage of radioactive materials.

Fluorescent screens made of inorganic phosphors are used with X-rays and cathode rays. The former are mainly of medical and metallurgical interest, but the cathode-ray tube is beginning to play a part in our daily lives. The cathode-ray oscillograph is now widely used in industry, and the variation of almost any quantity can be displayed on the screen. For instance, in the American Snow-Duplex spectrophotometer, the variation with wavelength of the absorption of a dye is shown.

The use of cathode-ray tubes in radar began with simple tubes indicating the distance of hostile aircraft, and was developed, among other purposes, to show a large plan of the ground over which an aircraft was flying.

The largest application of the cathode-ray tube, however, will be in the television receiver. A great deal is being written at present on television, and we need only mention here that public prejudice requires the receiver screen to be white, but that it could be made brighter if a greenish fluorescence were considered satisfactory. The receiver is normally used in a dimly lit room, and under these conditions the eye soon loses the sense of colour, so

the screen colour is really unimportant at present, but colour television must eventually arrive, and a white screen will then be essential. The best white phosphor mixtures at present are deficient in red, which appears either too dark or too yellowish.

Another rapidly expanding use of phosphors is in the fluorescent tubular lamps which have already been mentioned under light sources. In these lamps, an electric discharge passes through mercury vapour at a low pressure between electrodes coated with inorganic salts, which liberate electrons at a moderate temperature. Each electrode is a coil of tungsten wire, which must be heated by passage of a current to start the discharge. The tubes generally contain the gas argon in addition to the mercury vapour; this assists the passage of the discharge but takes no part in the light emission. Most of the energy emitted is in the ultra-violet, and this is converted by the coating of phosphor inside the tube into visible light. Depending on the constituents of the phosphor, the quality of the light can be varied, a "cold white" being preferred for industrial use, and a "warm white" for domestic purposes, while coloured tubes can also be produced for advertising or decorative effects.

There is a minor application of fluorescent substances merely as absorbers of ultra-violet radiation, their fluorescent emission being unimportant, in certain "sun-tan oils", which prevent the ultra-violet radiation from reaching the skin and producing sunburn.

#### TEXTILE APPLICATIONS

Although the fluorescent properties of dyes on textile fabrics have no doubt been used on occasions in the past purely as novelties, the widespread application of luminescence to textiles may be said to commence with the invention of "optical bleaching". Brief accounts of the history of the process have been given recently by Landolt<sup>2</sup> and Caspar<sup>3</sup>.

There are at present a number of optical bleaching agents on the market, whose properties are well exemplified by the products Uvitex RS and Uvitex WS (Ciba). The former is for application to cellulosic fibres, and the latter to wool, silk, nylon, and cellulose acetate.

UVITEX RS is readily soluble in water, neutral in reaction, and stable to chemical bleaching agents such as chlorine and hydrogen peroxide. It should not be used in conjunction with hydrosulphite or in an acid dyebath. Its dyeing and fastness properties are comparable with those of direct cotton dyes.

The general handling of Uvitex RS is similar to that of a cold-dyeing direct dye, such as Cotton Yellow CH. Greater exhaustion is obtained at low temperatures provided the time of application is sufficient: 30 min. at room temperature is recommended. Addition of Glauber's salt (5 lb. crystals per 100 gal.) is also necessary for exhaustion. As with direct dyes, very little levelling takes place at low temperatures, and free initial access of the solution to the material is essential. Also as with cold-dyeing dyes, sweating of Uvitex RS is liable to occur if the material is dried on a hot "can"; the temperature should be as low as possible.

Treated and untreated materials must not come into contact while wet, or "marking off" will occur.

A suitable strength of Uvitex RS is about 0.1-1% on the weight of material, but the amount which it is desirable to apply will depend upon the initial appearance of the material. For instance, where the material is initially a fairly good white, the brightest visual appearance is obtained when the white has been made distinctly bluish by application of Uvitex RS. Whether this is desirable or not will depend upon circumstances; a blue-white is particularly effective in combination with colours of the range from yellow to red. This applies particularly to the aftertreatment of discharge prints. In addition to application in the dyebath, Uvitex RS may also be applied by padding in a solution of  $\frac{1}{2}$ -10 lb. per 100 gal. followed immediately by drying. The other main division of use is in the brightening of pastel shades, as by this method shades of a brightness unapproachable by any other means are produced.

UVITEX WS is readily soluble in water, neutral in reaction, and unaffected by subsequent sulphur stoving. It has affinity for wool only in acid solution, and therefore must not be added to alkaline bleaches. Optimum results are obtained at 40-50°C. In considering the fastness to light, it must be borne in mind that wool fibres themselves are yellowed by light.

The proportion of Uvitex WS for best results is 0.5-5% on the weight of material, and this is applied with 5% of 40% acetic acid or 2-4% of 85% formic acid for 20-30 min. at 40-50°C. It is unnecessary to rinse before drying.

On furs, or sheep or rabbit skins, 4-6% Uvitex WS is applied with 6-8% formic acid at room temperature, hydroextracted, and dried without rinsing.

On silk, cellulose acetate, and nylon, the method of application is similar to that on wool, or alternatively the material may be padded in a solution of 2-20 lb. per 100 gal.

The uses of Uvitex WS fall naturally into the same two divisions as those of Uvitex RS, viz. the brightening of whites and the brightening of pastel shades. In the former class, the natural yellowish tint of the wool may be converted into a good white, while particularly striking examples of the latter class are the "baby pinks" and "powder blues".

To conclude the textile applications, we have already mentioned that a few dyes are strongly fluorescent; many others show a weak fluorescence which is insufficiently strong to be useful for special effects. Almost all classes of dyes include some which are fluorescent.

Several direct dyes show strong fluorescence in the range from yellow to red. Only one or two vat dyes show slight fluorescence, and this also applies, of course, to the Cibantine dyes when fully oxidised; these dyes in their soluble and unoxidised form are almost all strongly fluorescent. The disappearance of the fluorescence is used as an indication of complete oxidation.

Basic dyes on a tannin mordant do not fluoresce; neither do the azoic dyes, but an azoic dyeing may



show fluorescence if excess of naphthol is left in the material.

Among sulphur dyes, only the yellows are strongly fluorescent.

Of the dyes for wool and silk, several of the acid dyes show strong fluorescence in the range from yellow to red and also in the violet.

None of the chrome and Neolan dyes is strongly fluorescent. Many basics are fluorescent on wool and silk.

Several of the Cibacet range for cellulose acetate are fluorescent in the yellow-red part of the spectrum.

In conclusion, I must express my indebtedness to Messrs. The Clayton Aniline Co. Ltd. for permission to read this paper.

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#### Discussion

Mr. C. A. MILLS: Has any method yet been proposed to standardise or evaluate optical bleaching agents?

Mr. TAYLOR: Up to the present only comparative visual and colorimetric tests have been proposed; the standard of accuracy is not high.

Mr. R. J. ROBERTS: Goods treated with certain of these products have shown up very badly after a domestic wash.

Mr. J. G. GRUNDY: We agree that this is sometimes the case, particularly when the product has been used to mask a poor ground colour. But, provided that the right type is used, the luminescents do enable the bleacher to produce a more brilliant white than heretofore. The only complaint that we have consistently experienced arises when shirts are laundry-processed while the associated collars are washed domestically, producing a different shade.

Mr. ROBERTS: What I have in mind is rather additive yellowing due to decomposition of the product.

Mr. GRUNDY: Quite a number of different optical bleaches are being marketed; some are far from

blameless in this respect, and it behoves the processor to be careful in selection.

Mr. W. L. LANGTON: Is it possible to improve the poor wash-fastness of the luminescents by aftertreatment with a fixing agent, as may be done with certain direct dyes?

Mr. GRUNDY: This is a practical proposition. Both urea-formaldehyde and melamine resins have been found useful in this respect.

Mr. A. S. CLULEY: Is there any difficulty in levelling goods on which the luminescent is patchy?

Mr. GRUNDY: With many products applicable to wool this is no more difficult than in the case of ordinary level-dyeing acid dyes. Products used for cellulosic fibres are improved by a light scouring.

Mr. D. B. MCPHERSON: Does the fluorescence at the ultra-violet end of the spectrum increase photo-degradation of the goods?

Mr. GRUNDY: Prolonged exposure is necessary for the degradation of any fibre; as optical bleaches fade in the early stages, the effect would be negligible.

Mr. TAYLOR: In reply to Mr. Langton, certain of these agents can be incorporated in printing pastes, and are of particular value in discharge white styles.

Mr. S. N. BRADSHAW: Does the application of a luminescent for the purpose of brightening pale shades affect the light fastness of the dyeing?

Mr. GRUNDY: The light fastness of the dye is completely unaffected, but fading of the luminescent might give an apparent loss of depth due to restoration of some of the original dullness.

Mr. TAYLOR: As the optical bleaching agent fades first it might actually act as a protective.

Mr. BELFIELD: Most of the members present are familiar with the partial return of the ground colour in discharge prints. Will the use of a luminescent tend to prevent this?

Mr. GRUNDY: The question is extremely interesting in its possibilities. No such investigation has yet been carried out, but we will go into the matter, as this effect might indeed be found to obtain.

\*Tests made subsequently to the lecture have shown that luminescent compounds do not influence the properties of those dyes which have a tendency to return on exposure to light.

• Communicated

## WEST RIDING SECTION

Meeting held at the Great Northern Victoria Hotel, Bradford, on 11th April 1949, Mr. J. M. GOODALL in the chair

### Ancient and Modern in Milling and Scouring

C. O. CLARK

The name *Walker* arose because the original Walker quite literally walked upon cloth to cleanse or to full it. A similar process of trampling was used in the fur dressing trade until quite recently, and the description of it given by J. C. Sachs<sup>9</sup> in his book on furs is applicable in almost every detail to the manner in which, as we know from literature and excavations, cloth was fulled in Roman Italy and Gaul. Briefly, the cloth or skins were placed in a tub, and then a man got in it and, supporting his weight with his arms on the sides of the tub, proceeded to trample or mark time on the contents. It was naturally very warm work, and the men on the job wore little or no clothing. It has even been suggested that the sweat from the operatives helped to dress the leather. That human sweat is a good milling agent is known only too well from the way socks shrink or vests felt under the armpits. Which came first, cloth walking or fur trampling or kicking, is, as far as I have been able to gather, unknown.

Now the oldest milling and scouring agent we have, and the one the weight of which used far exceeds that of all other scouring and milling agents together, is water. In fact, from one point of view, all the other detergents and milling agents—soap, acid, sulphated and non-ionic products, etc.—only speed up or modify the effect of the water with which they are used. Formerly, and in France at least until well into the latter half of the eighteenth century<sup>4</sup>, pieces were cleansed before being treated in the fulling stocks by placing them at length in the bed of a river or mill stream and leaving them there for 8–15 days, changing them about from time to time to prevent them from always being in the same folds or exposing the same surfaces, which would cause them to acquire the so-called "flame" marks, i.e. streaks down the piece due to the effect of exposure to sunlight. To-day water alone is still the stain remover that has most uses and as such is the first the garment cleaner uses for spotting. Milling with water alone is practised to some extent even to-day, particularly in Scotland.

Fuller's earth or a similar earth or clay is the oldest detergent other than water used by the dyer and finisher of wool goods. Perhaps the very antiquity of fuller's earth may have led to its being the least investigated and certainly the least written-about agent used for processing wool. It appears to provide a classic example of a subject that everybody is supposed to know all about, so that it is considered of little use to write or publish anything about it. The only trouble is that, though it is blithely and often incorrectly assumed that everybody knows all about it, everybody has always thought so, and so little of value has ever

appeared in print. Time and time again one reads that the goods are earthed, but very rarely does any author say how, or even why, this is done.

In England the use of fuller's earth has been traced back for over 2000 years. In fact its use was considered, quite falsely I believe, to be one of the chief factors in making English-produced wool cloths the world's best, so that for centuries its export was forbidden under severe penalties, and was allowed only after the industrial revolution had started. During the nineteenth century vast amounts were exported to the Continent and North America for use by wool cloth dyers and finishers, yet no-one has ever even put on record an adequate account of the way in which fuller's earth was, and in some cases still is, used, let alone undertaken a proper investigation of its mode of action. Even to-day no-one has yet put forward a theory to explain why fuller's earth should act as a milling agent. This neglect of the subject is shown by the fact that not until 1929 was fuller's earth included in the monthly price list of chemicals published in our *Journal*, by which time its importance had greatly declined from what it was in 1900 and earlier. I took up the study of fuller's earth solely to collect details of its mode of use so that historians of technical developments would know not only when and where it was used but also, what is more important, why and how. It is a pity that most research into the history of our trades has been done by economists, whose interests were with the when and where and not with the why and how. Thus I started out with, and held until quite recently, the view that, despite the fact that fuller's earth was still used, e.g. for earthing indigo pieces, yet its use was on the wane and would not last long. However, Mr. Herbert à Brassard, in a talk he gave to the Huddersfield section in March 1949, suggested the use of fuller's earth to help in the milling and scouring of wool pieces with secondary alkyl sulphates. Thus there may be a new lease of life in store for fuller's earth in the wool industry.

The first use of fuller's earth cannot be traced, but during the whole of recorded history various earths have been used for cleansing textiles. "Fulling" is now synonymous with *milling*, but it was originally applied to the process of cleansing the cloth<sup>6</sup> which under the original system of "walking" on it necessarily involved felting and so what we obtain by milling a cloth. In the sixteenth century fulling mills were often known as *walk-milns*, and Thoresby<sup>10</sup> states that they were generally called *waugh* mills and the earth used for scouring was termed *walker-earth*. It is only comparatively recently that the word "fulling" has become divorced from the idea of cleansing<sup>8</sup>, although the main use of fuller's earth in the wool

dyeing and finishing industry is still purely and simply a cleansing operation.

For centuries English fuller's earth was regarded as unique, and the unequalled quality of English wool cloths was said to depend on it<sup>3</sup>—this was the occasion for the abovementioned ban on its export—although an occasional sceptic might write "in Holland and France, where they have no Fuller's earth, and yet make as fine Cloth as we do in England"<sup>1</sup>. This being so, it is all the more strange that the earliest mention I have been able to trace of its use is in 1656, when it was stated that without it "Clothing cannot be scoured from the Seame and Oyls, where with they must necessarily be wrought"<sup>2</sup> (it should be explained that by "clothing" was meant what we term *cloth* or *fabric*).

By the time any reliable technical information was put on record the ancient fulling had, by and large, become separated into the two processes of scouring and milling, even if these were done in the same or similar machines. It appears that by the end of the eighteenth century in the greater part of the wool cloth trade the chief scouring agent was stale urine with perhaps the addition of pig dung in this country and sheep dung in France. Why pig dung was used in preference to sheep dung in Britain, which was the world's largest sheep country (it is still the fifth), whereas the reverse was the case in France, is something for which I have so far been unable to find an explanation. The chief milling agent was soap, and fuller's earth was used as a light scour after milling, though dyers used it, as did their forefathers and as do their descendants at present, for scouring indigos or other dyeings which rub. It is a pity that this change in trade practice from using fuller's earth as the combined scouring and milling agent to its displacement as a scouring agent by urine and as a milling agent by soap appears never to have been put on record.

I am now going to wander from my main theme of fuller's earth to consider its supplanters. Soap as regards its use in the wool trade before 1800 has also been little written about, although again it is ancient and I suspect was more used than the existing literature would indicate. It was introduced to the Romans by the Germans, who used it not as a cleansing agent but as a hair pomade. For a long time its use was mainly as an unguent or a medicine so far as can be gathered from the scrappy references in the literature. Yet it may have been used for milling and scouring, although no record of such use remains, for in an Egyptian papyrus of the second century soap is mentioned as part of a dyeing recipe. We must not forget that soap as we know it depends on a supply of very pure soda, and that that was not available either cheaply or in large amounts until the end of the eighteenth century. One French writer of the eighteenth century<sup>4</sup>, referring to the use of soap in the then flourishing woollen industry in the south of France, mentions the black soap made from olive oil and the best cinders, in other words potash, the black presumably being due to the charcoal in the potash. The history of the use of soap in

the wool textile industry, from a technician's view-point of why and how, instead of the where and when which is all the historians have worried about so far, is an unworked field of investigation.

The use of plants such as soap wort is also very ancient, and the use of soap bark is still not unknown among indigo dyers. It would be idle to speculate on how decoctions of these plants came to be used or on how the properties of potash were first perceived. In the same way it is unknown how the detergent properties of stale urine came to be known; probably its use is very old, for the Eskimos, who retain many vestiges of prehistoric customs and uses, use it for washing their hair and cleaning their teeth. Its use was well known to the Romans, and the collectors of urine, *fullones* as they were called, became so prosperous that Commodus in A.D. 190 placed a special tax on them. It was also largely used in Florence when that Italian city was the world's most important centre of cloth finishing. Receptacles were placed at street corners, and the inhabitants of the city were expected to contribute to the supply of detergent for the city's source of richness and power. Some observer of that time has reported that the contributions of the gentlemen returning home from long evenings at the tavern were not particularly favoured by the foremen millers and scourers of the day. What was most in demand was that from the sober citizens and their wives who enjoyed their evening potion with a substantial meal, and then went to bed and well brewed their contribution before adding it to the common fund. There is scientific justification for this view, for the liquor with the larger nitrogen content would give the better detergent. That is by the way, but in this country stale urine, or *lant* as it was known, often made into really odoriferous mixtures with fermented pig dung and other ingredients, became increasingly of importance towards the end of the eighteenth century; round about 1800 its use was at its peak, after which it fought a losing battle with soda and soap. It died hard, however—I presume that it is now quite dead—for my colleague Mr. Edmund Wilson tells me that when he went to Ripley's in 1920 an old foreman there would persist in calling soda ash "urine", always referring to it as such. I myself in 1935 came across a firm in the Huddersfield area who were still using urine for scouring and who considered it a crime for any of the staff to waste any of their own production.

Thus all these detergents have lasted through the ages right into the times of the Igepons, Gardinols, Lissapols, Igepals, Lensex, and all that is embraced by the term *synthetic detergents* (although, of course, soap itself is a synthetic detergent), and now one of them, fuller's earth, is suggested to be used in combination with one of the latest products of modern applied science, truly a blending of ancient and modern.

Now to return to the main theme of this paper. There is no exact definition of fuller's earth—any marl or clay that will full cloth is entitled to be called by the name—but in Britain the name has in practice in the wool finishing industry come to be



restricted to the products obtained from Somerset and Surrey, although in other days other districts, notably Bedfordshire, Hampshire, and Kent, supplied it. Most of the so-called fuller's earths used for decolorising oils are not suitable for use with textiles.

Fuller's earth is, of course, a product which has never been produced to specification or subject to rigid analysis by the buyer; as long as it was free from grit and iron and had the right texture, the buyer was content. The usual method of testing was to stir it up in water and allow the mixture to settle. The sediment, and the less of it the better, was examined for grit, and a finger dipped into the supernatant liquor was expected to emerge covered with a film of the earth.

Fuller's earth was rarely used on raw wool, though Loebner<sup>7</sup> has recorded that in 1843 he used in Czechoslovakia a method he learnt in Belgium of cleansing spinning waste with it. He packed the waste into a vat and then placed a thick aqueous dispersion of Moravian fuller's earth over it. After the earthed waste had stood for 24 hr. workmen entered the vat and trod the waste and earth with their bare feet, after which the waste was rinsed with running water till the effluent was clear. The cleansed waste was soft and open, and spun much better than soda-cleansed waste, in particular giving much less fibre breakage during carding. Soda, however, did the job much more quickly and so ousted the use of earth.

I have been unable to find out anything about its mode of use in yarn scouring, but I have been informed that, up to 1940 at least, it was being used in Yorkshire for scouring carpet yarns. For this purpose the fact that it would be unaffected by any lime in the wool may have been of advantage, but this is pure speculation.

Its use in piece cleansing and finishing is a most complicated story, of which only certain features will be mentioned. In the thirteenth century, when Flanders produced the best wool cloths in the world, the cloth was placed for some days in a tub containing loamy earth in order to cleanse it before fulling. The use of soap or urine was forbidden under pain of imprisonment; thus clearly the use of soap was known in those days, and was doubtless practised. May not this prohibition and that of indigo later in England have had its basis in the difficulty of obtaining foreign exchange? After lying in the earth the cloth was carefully rinsed, and then fulled by being rubbed between two cards, the lineal ancestors of the modern hardening machine used in the felt industry.

One eighteenth century author<sup>4</sup> describes the following as the method of fulling: The dry piece was spread on the ground, evenly sprinkled with dry fuller's earth, and then placed in the stocks after being carefully folded or cuttled. The folding of the cloths was a delicate operation and had to be done most carefully. The machine was then run for 15 min. while water was slowly run into the cloth. The piece was then taken out, spread out, and examined to see if the fuller's earth was even on the cloth. If not, extra was added in the places where it was lacking, and the piece was

again placed in the stocks, and fulled as long as deemed necessary; then, with the machine still running, water was added more and more quickly until the effect became clear.

Two types of stocks were used. The one for cleaning had rounded hammers which were swung against the cloth, which was often in a horizontal trough. The one for fulling had hammers with sharp edges, their faces often being stepped or toothed, the particular hammers to be used varying with the type of cloth, and the hammers were dropped on to the cloth.

But the details and even the principles of the methods varied widely between different manufacturers. Indeed, to someone used to present-day practice, where except for small details methods have become largely standardised, it is bewildering to read eighteenth and early nineteenth century literature and try to systematise their methods. It cannot be done. At the one extreme there were finishers using methods familiar to all of us, who would not be entirely at a loss if they could enter a modern milling or scouring shed; at the other extreme there were finishers who were literally thousands of years behind what was technically possible in the light of the knowledge of their own days, knowledge which was put to practical use by some of their competitors. Reading French and English literature of those days leads me to think that one of the reasons for the success of the English cloth manufacturers was that they kept abreast of scientific progress. It was not that they alone had access to fuller's earth—that was to be found on the Continent, one of the reasons for the growth of the Flemish wool industry being that suitable earth occurred in Flanders—but that they made the best use of it.

Methods similar to these had been used for centuries and are used to-day to a small extent. At one time I was inclined to agree with earlier authors that the introduction of the roller milling machine was largely responsible for the decline in the use of fuller's earth for milling, on the ground that the cloth would suffer too severe abrasion—and fuller's earth does abrade the cloth, Speakman and Stott's<sup>5</sup> use of it for making wool non-felting depends on that very fact. However, it is quite clear that fuller's earth was on the decline long before the milling machine was invented. In the nineteenth century, at any rate, its two big uses were for earthing after dyeing and in the rinse after milling. It is a curious fact that, in much of the literature written in the last half of the nineteenth and the first half of this century, numerous references are to be found to the necessity of earthing after certain operations, particularly after the raising of beavers, on the ground that it was necessary to remove the soap and dirt brought out from the interior of the cloth. I had formed the theory that this was probably due to the fact that the soaps of those days were not as soluble as those we now have available and so were not completely rinsed from dense, heavily milled fabrics. On discussing this matter with Mr. Walter Stansfield, he told me that all this literature is wrong, for in his experience of dealing with that type of fabric

extending over sixty years, he had never known a piece to have to be earthed after raising. In view of that statement from a man of Mr. Stansfield's unrivalled experience, I believe that these statements in the literature are incorrect, and in fact I believe that the authors, wittingly or unwittingly, handed them on to one another, and that they originated with a French author in the middle of the eighteenth century. It is well known how, once a statement has appeared in technical literature, it is repeated and copied without thought as to whether it is right or wrong or often whether it has any basis of fact.

When natural dyes were the only ones available, all dyed material had, like the indigo pieces of to-day, to be given an earthing if fastness to rubbing was to be obtained. The introduction of synthetic dyes dealt that particular use of fuller's earth a severe blow and one that will probably prove mortal. But, curiously enough, the introduction of synthetic dyes, while it deprived fuller's earth of one of its main uses, opened up another to it. Many of the bright hues that were desired on wool, particularly on blankets for export, could be obtained only by the use of dyes which were not resistant to soap or alkali. For the scouring and milling of such fabrics fuller's earth had to be resorted to, and large amounts were used for this purpose. And here we are indirectly brought up against one of the reasons which may have resulted in a lessened use of fuller's earth—the problem of effluents and waste. In 1912 a Batley Carr firm who produced brilliantly coloured woollen rugs and shawls, and who for sixty years had used fuller's earth for scouring and milling them because the dyes that had to be used were fugitive to alkali, decided that they could no longer afford to use dear land for sewage purification and, in a dispute with the local authority, said they would have to discontinue the manufacture of these goods if they were not allowed to install a dry cleaning plant for them<sup>2</sup>. This reference to the use of dear land is significant, for there are other references to similar difficulties, which are understandable when it is realised that 1 ton of dry fuller's earth gives 10 tons of sludge deposited in the settling tanks. In a large mill these have to take up a great deal of space, and they have to be cleaned out periodically and the sludge has to be disposed of. Schemes for recovering the dye, notably indigo, from such sludges have been proposed, but have never come to anything. No record of the recovery and re-use of the earth can be found; presumably fresh earth was too cheap for it to be considered.

The last real home in the wool textile trade that was left to fuller's earth in 1939 was in the earthing of indigo and other dyeings which have come up faulty to rubbing. Even in this field its use was being challenged, for products of the type of Igepon A are better than fuller's earth for after-treating indigos so long as the cloth will stand being treated at 110°F. Now Mr. à Brassard comes along with his idea of using one of our newest detergents and one of our oldest in combination, particularly for milling. Fuller's earth has often in the past been used in conjunction with other detergents, notably soap bark and ammonia. But why did we all leave such an obvious suggestion for Mr. à Brassard to make? Was it that it was too simple and staring us in the face all the time? Be that as it may, we can but account it as certainly an original and, it may prove, a valuable contribution to our age-old industry. There is a similar case of an obvious method of use being ignored in the history of fuller's earth. In the literature there is just one isolated reference to the fact that fuller's earth is an admirable scouring agent to use in an acetic acid bath. Have not non-ionic detergents been suggested for use in acid liquors for the last 12–15 years, and may not a combination of them with fuller's earth be useful? The point is that the previous reference to scouring with fuller's earth in acid liquors passed unnoticed and certainly without any recorded investigation. Why it was never acted upon is queer, for I know of several finishers who often acidify certain classes of goods after scouring them, e.g. white effects in black cloths show up much more clearly if the goods are brought just on to the acid side by treating them in a weak bath of acetic acid.

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## COMMUNICATION

## A Direct-reading Photoelectric Spectrophotometer

T. B. DAVENPORT

A non-recording photoelectric spectrophotometer suitable for reflectance measurements over the spectral range 4000–6500 Å. is described. The instrument is compact and accurate, operates from A.C. mains, and is simple to use.

## INTRODUCTION

The appearance on the British market of several types of photoelectric spectrophotometers seems to indicate an increase of interest in accurate colorimetric measurement, and it therefore seems that a description of an instrument designed by the author some years ago may prove of interest to workers in this field. No special virtues are claimed for the instrument apart from those listed in the summary, but it should be noted that it may be constructed in the normal laboratory workshop, has a low initial cost with negligible upkeep costs, and is extremely robust.

with the optical system. Between  $L_4$  and  $A_1$  a modulator disc  $M$  is mounted on the spindle of a small constant-speed electric motor so as to provide 1000 cycles/sec. modulation of the spectral beam, which is finally focussed in the plane of an aperture  $A_2$  cut at a diametrically opposite point to  $A_1$  in the wall of the sphere.

The material of which the spectral reflection characteristics are to be examined is held over this second aperture, and light reflected from the sample is integrated by the whitened interior of the sphere and finally passes out of the sphere through a third aperture  $A_3$  cut in the wall of the sphere so as to

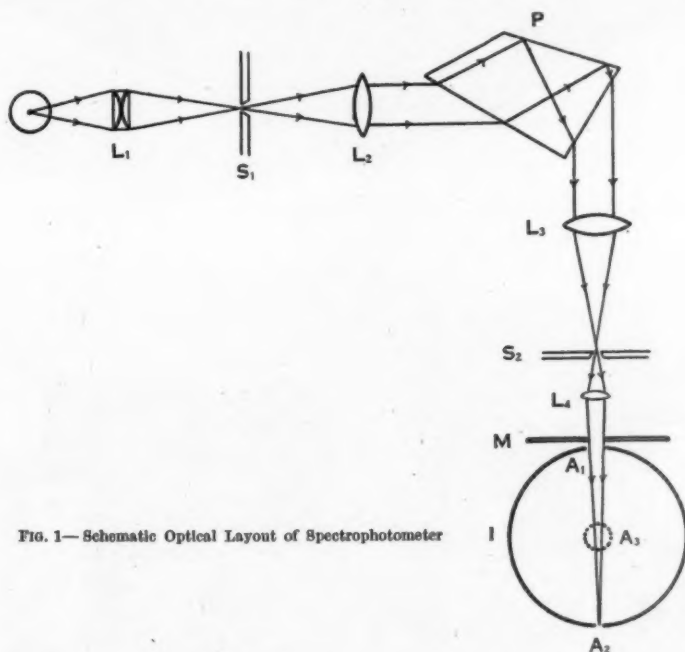


FIG. 1—Schematic Optical Layout of Spectrophotometer

## PRINCIPLE OF SPECTROPHOTOMETER

A schematic illustration of the optical system is shown in Fig. 1. Light from a straight line filament lamp is condensed by a double planoconvex lens combination  $L_1$  on to a symmetrically adjustable optical slit  $S_1$ , and collimated after passage through the slit by an achromatic lens  $L_2$ . After passage through a constant-deviation prism  $P$ , the dispersed beam is focussed by a second achromatic lens  $L_3$  on a second slit  $S_2$ , and the narrow band of spectral light passed by  $S_2$  is focussed by a fourth lens  $L_4$  so as to pass through an aperture  $A_1$  in the wall of an 8 in. diameter sphere  $I$  mounted axially

lie at  $90^\circ$  to the diameter joining apertures  $A_1$  and  $A_2$ . Outside the sphere and adjacent to  $A_2$  is mounted a photomultiplier tube in such a position as to receive on its cathode the maximum integrated light from the interior of the sphere. The 1000 cycles/sec. alternating voltage developed across the load resistance of the multiplier tube is fed to a three-valve amplifier followed by a peak-reading valve voltmeter, the indicating instrument being a 100- $\mu$ a. (full-scale deflection) moving-coil meter with a five-inch scale. It is thus possible to compare the amounts of light reflected by given samples of material at any given point within the

wavelength range of the instrument by comparing the corresponding meter readings. In general the instrument is set to give a full-scale deflection when examining a standard magnesium carbonate surface and zero deflection when examining a matt-black cavity. With this in view the scale is calibrated to read percentage reflection, enabling direct readings to be taken on substitution of the sample.

sides being enclosed by  $\frac{1}{8}$ -in. sheet brass with the exception of the sloping panel at the front, on which are mounted the meter, the zero control, and the escutcheon for the wavelength drum. The panel is  $\frac{1}{4}$  in. thick Tufnol sheet. The whole unit is made more rigid by a cruciform structure of 1-in. cross-section brass bar running externally along the diagonals of the baseplate. The side panels are

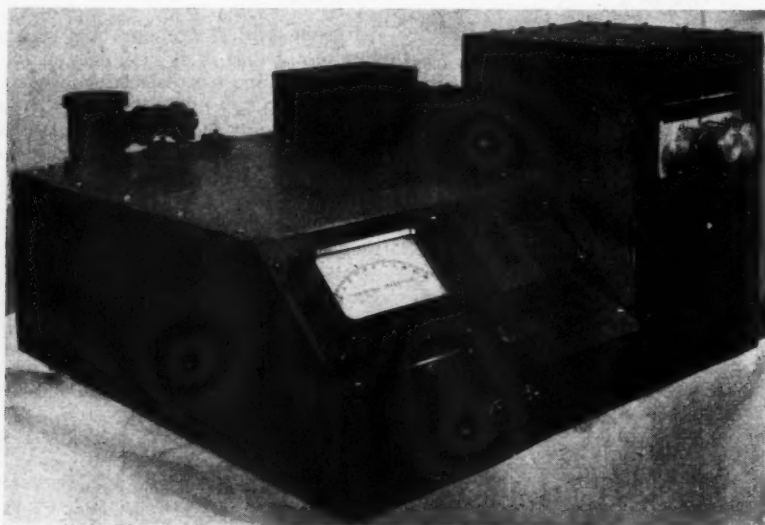


FIG. 2—Completed Spectrophotometer

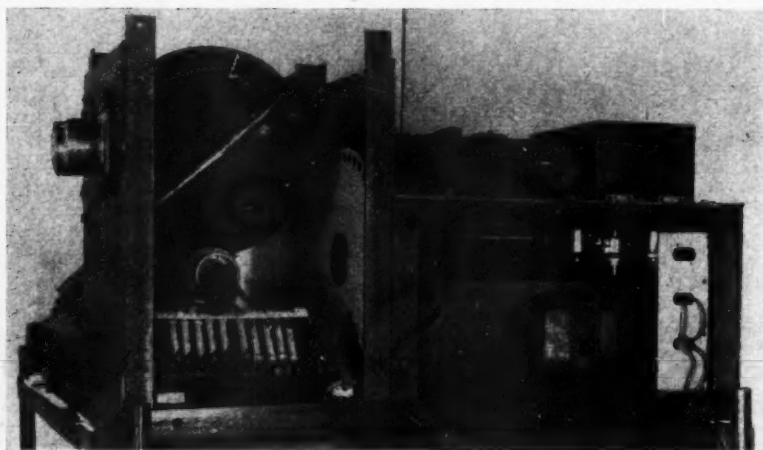


FIG. 3—Photograph showing Integrator Sphere and Modulator

Power for operation of the multiplier tube, amplifier, and valve voltmeter is provided by a suitable power pack operating from a constant-voltage transformer supplied from the A.C. mains.

#### GENERAL CONSTRUCTION (Fig. 2 and 3)

The framework of the instrument is constructed in 1-in. angle steel, base, top (optical bed), and

secured to the framework by 2BA screws, and may be removed easily to give access to the interior, in which are housed amplifier, power pack, lamp transformer, mechanism for rotating the prism table, modulator disc and motor, integrating sphere, and the photomultiplier with its associated bank of resistors.

The major portion of the optical system is mounted externally, the prism and prism table

being enclosed by a removable case, from which is run the tubular housing for lens  $L_3$ , slit  $S_2$ , and lens  $L_4$  (Fig. 1). This tubular housing ends in a light-tight joint at the elevated section of the case in which are housed the integrating sphere and associated components.

#### OPTICAL SYSTEM

The lamp employed is a standard 6-volt, 36-watt, double-contact car headlamp with linear filament and is mounted in a cylindrical lamp housing of conventional design together with the double planoconvex condenser system. It is found that the standard type of lamp socket is unsatisfactory, since the coil springs actuating the two contact plungers take the full circuit current. This causes the springs to overheat and become

This cylinder is a tight sliding fit in a tube mounted in an annulus secured to the backplate of the entry slit, and may be locked in the correct position for collimating by a grub screw through the wall of the tube. The entry slit and collimating lens therefore form one rigid unit.

The prism table (Fig. 5) is formed from two shallow cylindrical brass blocks  $A$ , the upper block being capable of rotation on a large-diameter thrust ball-race  $B$ , recessed into the adjacent faces of the blocks, the lower block being screwed to the optical bed  $C$ . A length of  $\frac{3}{8}$  in. diameter silver steel rod  $D$  expanded into the rotating member passes through the lower block and optical bed and is journaled in a ball-race  $E$ , suitably mounted on a horizontal member  $F$  separated from the underside of the bed by two stout brass pillars  $G$   $1\frac{1}{2}$  in.

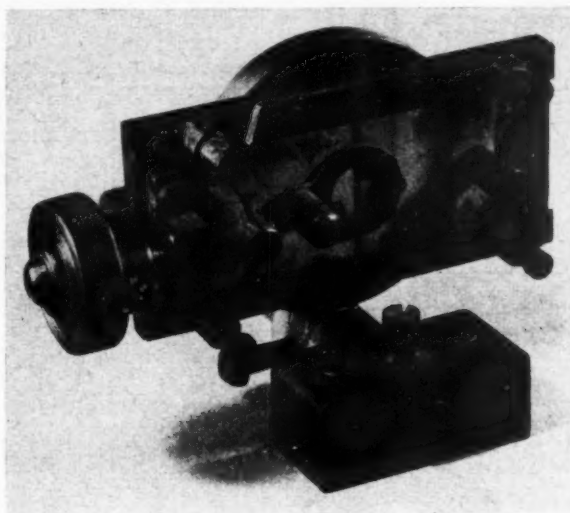


Fig. 4—Entry Slit

detempered, leading to decreased contact pressure and consequent irregularity in burning of the lamp. Accordingly a simple socket constructed in brass and Tufnol with springs which do not carry current is employed.

The entry slit (Fig. 4) consists of an  $\frac{1}{8}$  in. thick brass backplate with  $\frac{1}{16}$  in. thick jaw guides bevelled to  $45^\circ$  to accommodate the two  $\frac{1}{16}$  in. thick steel jaws, the optical edges of which are bevelled in the usual manner. Spring steel strips tend to hold the jaws apart, and the actuating screw is cut with two threaded sections; one left-hand and the other right-hand, passing through correspondingly threaded brass pillars mounted on the jaws in such a manner that rotation of the screw adjusts the slit width symmetrically. Focussing of the lamp filament image on the entry slit is facilitated by mounting the slit on a massive brass collar sliding on a short length of  $\frac{3}{8}$  in. diameter silver steel rod journaled in brass blocks secured to the optical bed. The collimating lens  $L_2$  (Fig. 1) is mounted with litharge and glycerol cement in the recessed end of a short cylinder.

high. Between the underside of the bed and the horizontal member two brass bosses  $H$  and  $I$  are situated, the inner boss being secured to the silver steel rod by a recessed screw  $J$ , and the outer riding tightly round the inner and having secured to its periphery the arm  $K$ , which extends to the table-driving mechanism.

A narrow key  $A$  (Fig. 6), running axially on the inner boss  $B$ , projects into a wider keyway  $C$  cut in the adjacent face of the outer boss  $D$ , where two screws  $E$  and  $F$  make it possible to lock the bosses against mutual rotation. This arrangement permits a rapid and accurate wavelength adjustment to be effected during initial calibration of the instrument.

The mechanism transmitting motion to the arm actuating the prism table (Fig. 7) consists of a small phosphor bronze cylinder  $A$ , drilled and tapped axially to form a nut which rides on a short length of  $\frac{1}{8}$  in. diameter silver steel rod  $B$  (40 threads per inch), journaled in adjustable thrust bearings  $C$  and  $D$  between rigid end-plates  $E$ . A  $\frac{1}{8}$  in. diameter silver steel rod  $F$ , running parallel to the

threaded rod *B*, engages in a radial slot milled in the periphery of the nut, preventing its rotation and thus translating a rotation of the threaded rod into a to-and-fro motion of the nut. A small hardened steel rod *G* projects radially from the phosphor bronze nut and engages with a hardened

sprockets *N* and *O*. The wavelength drum *M* is turned from block Perspex and measures 5 in. in diameter by  $1\frac{1}{2}$  in. wide, having brass bushes and set-screws to secure it to the  $\frac{1}{4}$  in. diameter silver steel rod *L*, about which it may be rotated. A strip of white celluloid  $1\frac{1}{2}$  in.  $\times$  15 in. is secured

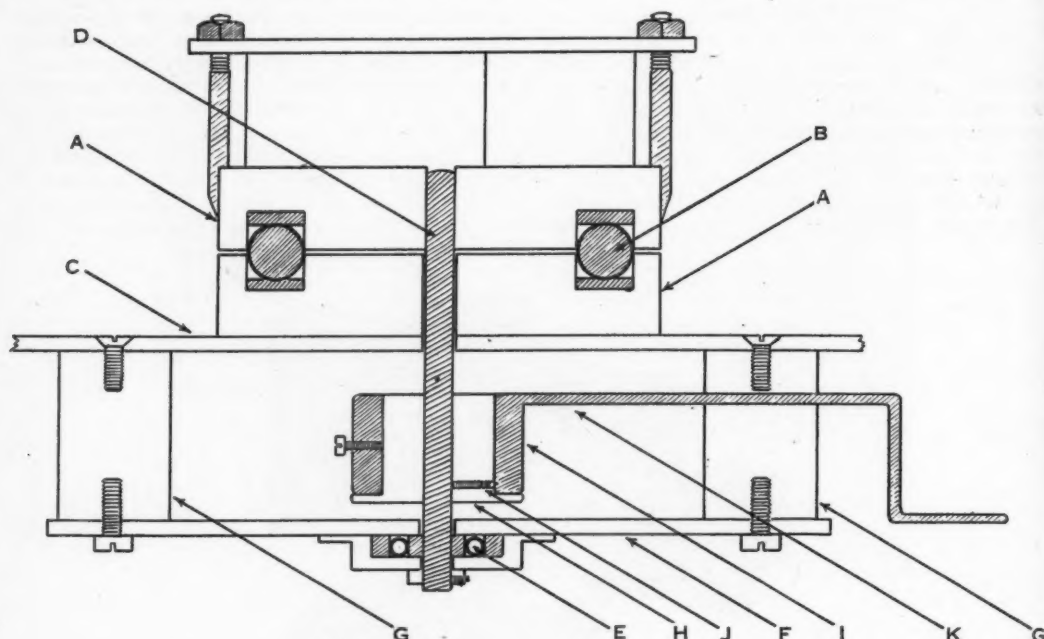


FIG. 5—Cross-section of Prism Table Assembly

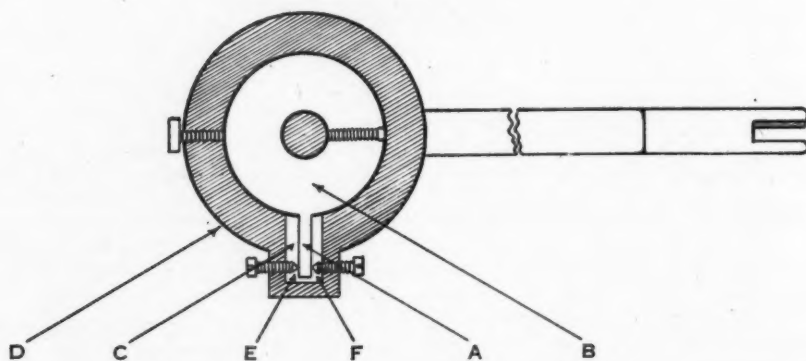


FIG. 6—Detail of Prism Table Actuating Arm, showing Fine Adjustment

steel insert at the extremity of the arm actuating the prism table, which is suitably spring-loaded against the motion.

Coupling between the prism table drive and the wavelength drum (Fig. 7) is effected by  $\frac{1}{8}$  in. diameter silver steel rod *H* running parallel to the underside of the optical bed *I* through three sets of accurately aligned ball races *J* and terminating in a right-angle reduction gear *K* on to the axis *L* of the drum *M*. The transmission rod is coupled directly to the wavelength control by chain and

round the circumference to form a scale for subsequent calibration in angstroms, whilst a deep circumferential recess *P* in the drum permits scale illumination from the rear.

The lenses *L*<sub>3</sub>, *L*<sub>4</sub> and the exit slit (Fig. 8) comprise a single rigid unit built into  $2\frac{1}{2}$  in. diameter brass tubing extending from the hinged cover enclosing the prism table to the section of the instrument case in which is housed the integrator sphere. The exit slit is constructed in a similar manner to the entry slit, but the jaws *A* are radiused



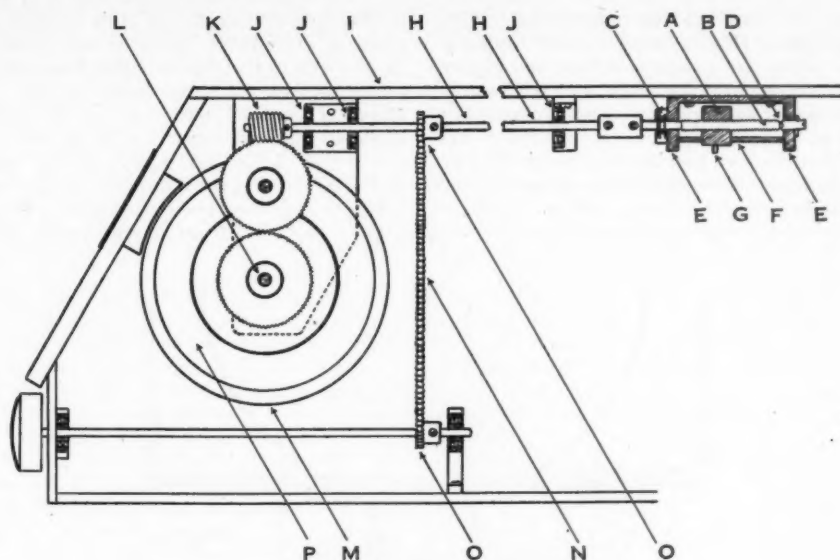


FIG. 7—Wavelength Drum and Transmission

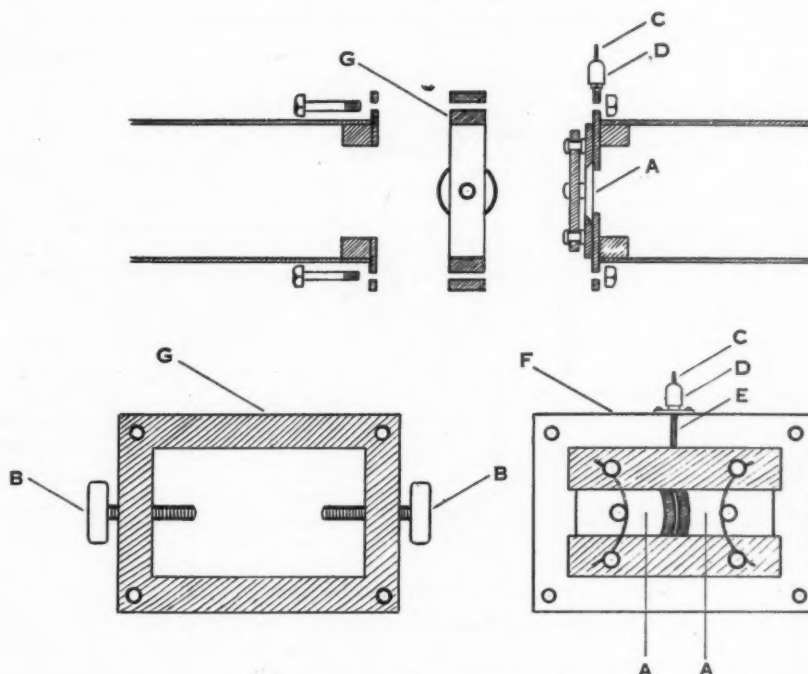


FIG. 8—Exploded Diagram of Exit Slit

to compensate for the spectrum curvature and are individually adjustable by two knurled screws *B* set in opposite sides of the brass frame *G*.

A steel needle *C*, ground flat towards its tip, is held in a small chuck *D* situated on the upper edge of the slit backplate, and passes down a shallow groove *E* in the backplate *F* to form an index in the plane of the slit, against which spectral lines may be set during calibration.

Modulation of the light beam is effected by an 8 in. diameter opaque celluloid disc (Fig. 3) perforated along a circumference near its periphery by circular apertures. The spacing between adjacent apertures is equal to the width of the beam, whilst the aperture diameter equals the height of the beam. The disc is mounted by means of a brass bush on the spindle of a small constant-speed electric motor supported firmly on a brass pillar

secured to the base of the instrument. The integrating sphere (Fig. 3) is spun from copper in two halves, which are joined by drilled and tapped flanges. From one half, a segment 4 in. in diameter is removed, and a brass plate with a symmetrically disposed 4 in. diameter aperture is soldered to the sphere so that the two apertures coincide (Fig. 9). Rigid positioning of the integrator sphere is thus ensured by mounting the plate against the front interior face of the spectrophotometer case.

The specimen holder (Fig. 9) consists of a brass plate *A*,  $\frac{1}{8}$  in. thick, riding in two brass guides *B* on the exterior of the integrator sphere compartment, so that the three short tubes *C*, *D*, and *E* mounted on the plate may be brought in turn opposite the exit aperture *F* of the integrator sphere *G*. A ball and spring in the upper guide and three appropriate notches in the brass plate ensure correct location of the tubes. The left-hand tube *C* houses the zero reflectance standard (a

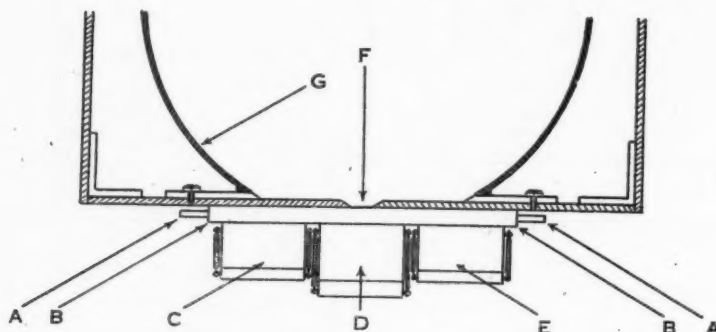


FIG. 9—Integrator Sphere, and Pattern and Standards Holders

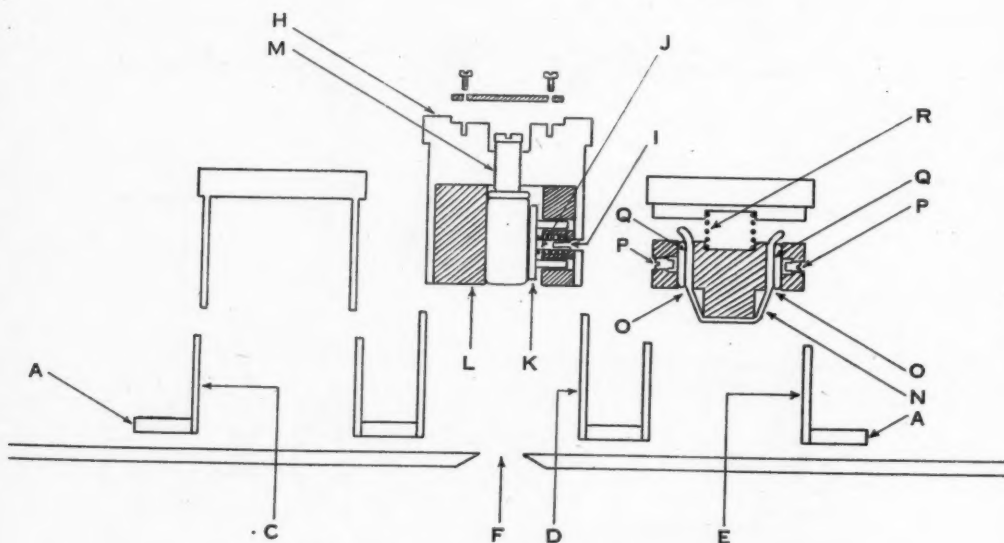


FIG. 10—Section showing Construction of Pattern and Standards Holders

An R.C.A. 931 A photomultiplier is mounted in a short length of  $1\frac{1}{2}$  in. diameter brass tubing secured to the wall of the integrator sphere via a brass annulus milled radially on one face to receive the multiplier case and shaped on the opposite face to fit the curvature of the sphere, appropriate windows being cut in the walls of the sphere and photomultiplier case to permit maximum illumination of the photocathode by the integrated light. All light-integrating surfaces are coated with a good matt-white paint and subsequently smoked with magnesium oxide.

cylindrical cavity with matt-black interior), the middle tube *D* houses the 100% reflectance standard (a magnesium carbonate block), and the right-hand tube *E* the mounted sample to be examined.

The magnesium carbonate block holder *H* (Fig. 10) is machined so that the clearance between its front face and the backplate of the integrating enclosure is not greater than 0.001 in. The magnesium carbonate block is mounted by inserting a 6BA bolt in the appropriately tapped hole *I* in the spring-loaded centre guide *J* and retracting the

assembly till there is sufficient clearance between the plate *K* and the block *L* to permit insertion of the magnesium carbonate block. The 6BA bolt is then removed, when the block will be gripped firmly between *K* and *L*. On rotating the screw *M*, the face of the magnesium carbonate block is raised slightly above that of its holder, and a razor blade may be run slowly across the block until the two faces are perfectly flush. When the face of the block loses its freshness it is a simple matter to provide a new surface by repetition of the above process.

The sample holder shown (Fig. 10) is designed for textile fabrics, leather, paper, etc., and is obviously unsuitable for use in examining other samples such as metals, rubber, and clays, but it is thought that the tubular form of mounting adopted will enable other types of holders to be accommodated with the minimum of trouble. The sample *N* is mounted by threading it through the slots *O*, and clamping in position by means of the short bolts *P* bearing against the plates *Q*. The light spring *R* ensures that the pattern is maintained in gentle contact with the sphere backplate. Undue pressure will tend to change the reflection characteristics of the sample, so that it is important that the lightest spring consistent with good contact is employed.

In the foregoing account no details of focal lengths, apertures, etc. have been included in the paragraphs dealing with the monochromator. This omission is deliberate, since the instrument was constructed under wartime conditions, when the restriction on optical components rendered it impossible to design with a view to optimum performance. As some guide to intending constructors, however, it may be noted that adequate sensitivity is obtained in the present instrument by using an exit slit width corresponding to 50 A. at 4000 A.

#### ELECTRICAL SYSTEM

The 1000 cycles/sec. signal developed across the photomultiplier load resistor is fed through shielded cable to a three-stage amplifier and valve voltmeter (Fig. 11) assembled on a brass chassis measuring  $10 \times 5 \times 3$  in. mounted within the framework of the spectrophotometer, so that removal of a side panel immediately exposes the underside of the assembly to facilitate servicing. The attenuator *R*<sub>6</sub>, inserted between the first and second stages of the amplifier to minimise contact noise at the output, is operated through an epicyclic reduction drive by rotation of the 3 in. diameter instrument knob situated on the extreme left of the control panel. Valves *V*<sub>1</sub>, *V*<sub>2</sub>, *V*<sub>3</sub> are of "all-metal" construction tested for freedom from microphonic characteristics, and all resistors employed are high grade with the common aim of obtaining as high as possible a signal : noise ratio from the amplifier.

For this reason a bandpass filter is inserted between the second and third stages of the amplifier. The attenuation characteristics of this filter and the previously mentioned precautions enable a signal : noise ratio of 500 : 1 to be obtained even when the instrument is being operated over its least sensitive spectral region. The filter

employs air-cored inductances and paper condensers, the entire unit being assembled on a Perspex former 2 in. in diameter by 5 in. high, the inductances being mounted at opposite ends of the former and separated from each other by the bank of condensers.

In order to ensure that a linear response is obtained from the amplifier and valve voltmeter the circuit values are adjusted so that a full scale deflection is obtained on the microammeter *M* (Fig. 11) when 2 v. is applied to the grid of *V*<sub>5</sub>. Under this condition the anode swing of *V*<sub>3</sub> corresponds to 20 v. and 100 v. is applied across the diode *V*<sub>4</sub>. *V*<sub>3</sub> and *V*<sub>5</sub> are therefore working well within the limits of their linear characteristics, and "bottom bend" distortion is reduced to a minimum for the diode *V*<sub>4</sub>. Tests carried out with a beat-frequency oscillator and calibrated attenuator feeding the amplifier input gave an absolutely linear relation between input and microammeter *M* deflection.

The two halves of the double triode cathode followers *V*<sub>5</sub> are adjusted initially with both control grids earthed to give zero deflection of the microammeter *M* by filing the appropriate cathode resistor. When an accurate balance of cathode voltage has been obtained the treated resistor is given a complete coat of insulating varnish.

The wire-wound potentiometer *R*<sub>21</sub> comprises the "set zero" control by providing a small variable positive bias which may be applied to the cathode of the diode *V*<sub>4</sub>. With the very low noise level which obtains on this amplifier the "set zero" control is a refinement, the omission of which affects the accuracy of the instrument very little unless low reflectance readings are being taken.

Power pack design is conventional (Fig. 11), the units for supplying 250 v. D.C. and 6.3 v. A.C. to the amplifier being grouped on the same shallow brass chassis as the unit which supplied 1250 v. D.C. to the photomultiplier. 3000 v. A.C. is supplied to the single-wave rectifier, thus permitting a high value of smoothing resistor *R*<sub>33</sub> to be employed, which together with a value of 1 μF. for the smoothing condensers *C*<sub>21</sub> and *C*<sub>22</sub> results in the ripple-free supply which is essential for satisfactory operation of the multiplier.

Both power packs, the modulator motor, and the lamp transformer are coupled to the 230 v. A.C. mains through a 250-w. constant-voltage transformer.

#### CALIBRATION OF MONOCHROMATOR

The 15 in. long celluloid scale surrounding the wavelength drum is dismounted and marked in millimetre divisions over its entire length using a fine pen and Indian ink. The scale is then replaced and, the entry slit being illuminated by a small neon lamp for the range 6500–5396 Å. and by an argon lamp for the remainder of the range, calibration is carried out in the usual manner, setting the standard spectral lines against the exit slit index. Scale readings are then plotted against wavelengths to give a calibration curve, interpolation of further points being made on the more sparsely populated portions of the curve using Hartmann's formula.

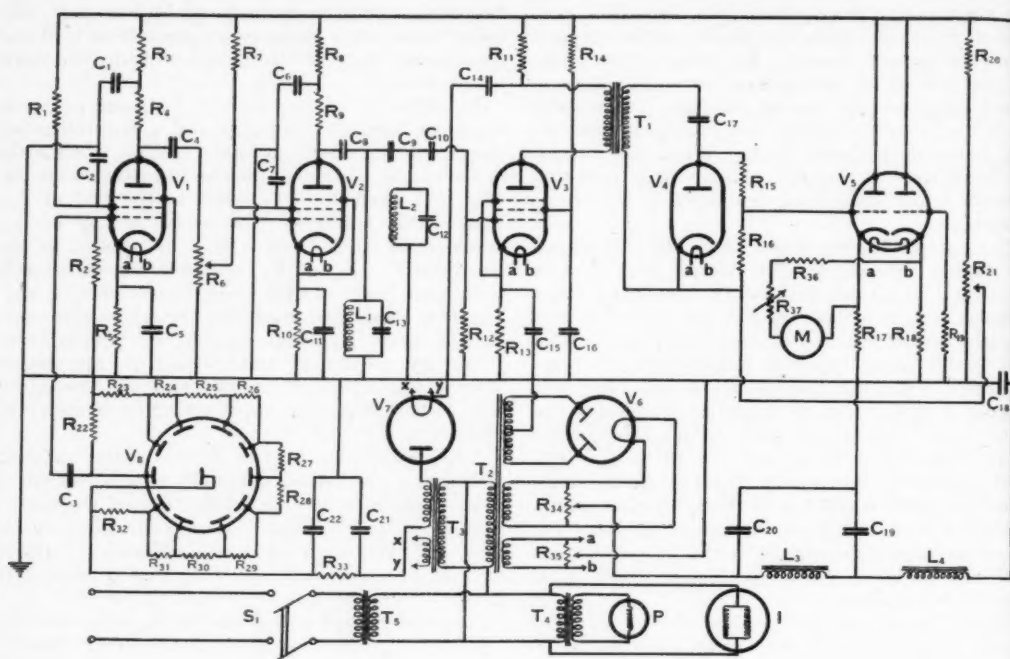


FIG. 11—Circuit Diagram of Spectrophotometer

Capacitances  
(microfarads)

$C_1$ ...	1.0
$C_2$ ...	0.1
$C_3$ ...	0.01
$C_4$ ...	0.01
$C_5$ ...	25
$C_6$ ...	1.0
$C_7$ ...	0.1
$C_8$ ...	0.016
$C_9$ ...	0.006
$C_{10}$ ...	0.016
$C_{11}$ ...	25
$C_{12}$ ...	0.29
$C_{13}$ ...	0.29
$C_{14}$ ...	1.0
$C_{15}$ ...	25
$C_{16}$ ...	0.1
$C_{17}$ ...	0.1
$C_{18}$ ...	8.0
$C_{19}$ ...	8.0
$C_{20}$ ...	16.0
$C_{21}$ ...	1.0
$C_{22}$ ...	1.0

(5000-v. test)

Resistances  
(ohms)

$R_1$ ...	$1.5 \times 10^6$
$R_2$ ...	$100 \times 10^3$
$R_3$ ...	$50 \times 10^4$
$R_4$ ...	$250 \times 10^3$
$R_5$ ...	$2 \times 10^3$
$R_6$ ...	$250 \times 10^3$ (wire-wound)
$R_7$ ...	$1.5 \times 10^6$
$R_8$ ...	$50 \times 10^3$
$R_9$ ...	$250 \times 10^3$
$R_{10}$ ...	$2 \times 10^3$
$R_{11}$ ...	$25 \times 10^3$
$R_{12}$ ...	$20 \times 10^3$
$R_{13}$ ...	$2 \times 10^3$
$R_{14}$ ...	$1.5 \times 10^6$
$R_{15}$ ...	$250 \times 10^3$
$R_{16}$ ...	$5 \times 10^3$
$R_{17}$ ...	900
$R_{18}$ ...	900
$R_{19}$ ...	$5 \times 10^3$
$R_{20}$ ...	$250 \times 10^3$
$R_{21}$ ...	500 (wirewound)
$R_{22}$ ...	$100 \times 10^3$
$R_{23}$ ...	$50 \times 10^3$
$R_{24}$ ...	$800 \times 10^3$ (10 watt)
$R_{25}$ ...	60
$R_{26}$ ...	60
$R_{27}$ ...	$25 \times 10^3$
$R_{28}$ ...	$2 \times 10^3$ (wire-wound)

Inductances  
(henries)

$L_1$ ...	0.16
$L_2$ ...	0.16
$L_3$ ...	50
$L_4$ ...	50

Valves	
$V_1$ — $V_3$ each	6J7
$V_4$ ...	6H6
$V_5$ ...	6F8
$V_6$ ...	80
$V_7$ ...	U17 (Osram)
$V_8$ ...	931A Photomultiplier (R.C.A.)

## Transformers

$T_1$	5:1 Step-up (primary inductance 50 H.)
$T_2$	Primary 230 v. Secondaries 250-0-250 v., 60 ma.; 6.3 v., 3 amp.; 5 v., 2 amp.
$T_3$	Primary 230 v. Secondaries 3000 v., 20 ma.; 4 v., 3 amp.
$T_4$	Primary 230 v. Secondary 6 v., 6 amp.
$T_5$	Constant-voltage, 250 w. (Advance Components Ltd.)

- $I$  Fractional-h.p. induction motor  
 $M$  Moving-coil meter, 100  $\mu$ a. full scale deflection (Taylor Electrical Instruments Ltd.)  
 $P$  Double-contact auto bulb, 6 v., 30 w.  
 $S$  Double-pole single-throw Q.M.B. switch



From the calibration curve the celluloid scale is then inscribed at 100-Å. intervals over the range 6500–4000 Å. using a sharp-pointed instrument. Finally the original millimetre graduations are washed off, and the wavelength calibration marks filled in again using Indian ink and a fine pen. After the scale has been replaced on the wavelength drum, a check is made against any well defined spectral line, and any small error made in replacing the scale corrected by means of the fine adjustment previously described.

#### OPERATION

The instrument is put into operation by depressing the switch  $S_1$  (Fig. 11) situated on the control panel and is ready for use almost immediately. With the wavelength drum set to 4000 Å. the standard white is aligned in the monochromator beam, and the attenuator control set to give a 100% reflection reading on the meter. The standard white is then replaced by the 0% reflection cavity, and the "set zero" control is operated to give zero deflection on the meter. Replacing the standard white, a check on the 100% reading is made, using the "fine" control ( $R_{37}$ , Fig. 11) to correct any slight discrepancy. Sliding the sample into position will now enable its reflectance to be read directly from the meter.

The wavelength drum is now set to 4100 Å., the standard white replaced, and the attenuator adjusted to give a 100% reflection reading. The reflectance of the sample may now be determined by substituting it in the beam and reading directly

from the meter, the zero check being necessary only at infrequent wavelength intervals. Facility in operation is soon acquired, and readings for a complete spectral reflection curve at 100-Å. intervals may be obtained within 10–15 min.

It should be noted that, although the spectrophotometer was designed for use as a reflection instrument, it may be employed perfectly satisfactorily to measure spectral transmission. In this case the standard white remains permanently in the monochromator beam, and the sample is placed in the collimated beam prior to its entering the prism, zero transmission being obtained by interposing an opaque stop in this same beam.

The transmission curve of a didymium glass filter measured in this manner is practically identical with the curve obtained from the General Electric recording spectrophotometer, the slight broadening of the peaks at longer wavelengths being attributable to the somewhat greater slit widths employed in the present instrument towards the red end of the spectrum.

A check of repetition accuracy has been made over the whole range of reflectance values, and it is found that deviations lie either within a 4.8% range or within the limits of 0.69 scale division (full scale = 100 divisions), whichever is superior.

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(Received 11th June 1949)

## Notes

### Proceedings of the Council

At a meeting of the Council, held at the offices of the Society, 32–34 Piccadilly, Bradford, on 11th January 1950, the proceedings included the following items of interest—

**DIPLOMA COMMITTEE**—It was decided to form a small Diploma Committee, on which Professor W. Bradley, Mr. C. O. Clark, Dr. R. L. Elliott, Mr. G. E. Holden, Mr. G. G. Hopkinson, Mr. W. Penn, Mr. F. Smith, and Professor J. B. Speakman were invited to serve.

**NOMINATION OF OFFICERS**—Mr. H. Jennison and Mr. J. Barritt were nominated for re-election as Honorary Treasurer and Honorary Secretary respectively.

**LISTS OF COMMITTEES**—It was decided that in future the composition of Council, committees, etc. should be published in the June issue of the *Journal*, but that official notices and lists of medals and awards should continue to appear in the January issue.

**MEMBERSHIP**—Seventeen applications for ordinary, and one for junior, membership were approved.

### Meetings of Council and Committees February

Council—8th                      Finance—8th  
Publications—14th  
Colour Index Editorial Panel—20th  
Vat Dyes—1st  
Summer School—10th  
Fastness Tests—17th  
Fastness Tests (Bradford Subcommittee)—13th

### Lectures on the Chemistry and Physics of Cellulose and Proteins (with special reference to Fibres)

A course of twenty lectures will be given at Bradford Technical College on Mondays and Thursdays at 7.15 p.m., from May 1st to July 6th inclusive. The lectures will be of an advanced nature, special emphasis being given to recent work and applications, and the course will include demonstrations and practical work. Forms of application, to be obtained from the Principal of the College, should be completed and returned by 15th April 1950.

### British Industries Fair

The British Industries Fair will be held in 1950 on May 8–19th at Olympia and Earls Court, London, and Castle Bromwich, Birmingham.

## New Books and Publications

### The Aromatic Diazo-Compounds and their Technical Applications

By K. H. Saunders. 2nd edition 1949. Pp. xi + 442. London: Edward Arnold & Co. Price, cloth, 50s. 0d.

The first edition of this book, which appeared in 1936, summarised up to that date the vast literature relating to the chemistry and uses of diazo compounds, a subject which had been neglected by book writers since the appearance in 1920 of Dr. J. C. Cain's second and last edition of *The Chemistry and Technology of the Diazo-Compounds*. It was one of the most welcome books of its type, and now that fourteen years have elapsed since it appeared, the demand for a second edition has been overwhelming. During the long interval, so much new work has appeared that this latest effort consists of twice as many pages as the first edition. Moreover, the concluding lament of the author in his first edition, that "the non-existence of any school devoted to a steady if small volume of research on diazo-compounds is to be regretted", will be seen to have borne fruit when a study of the author index is made.

The layout of the chapters in the new volume is very similar to that of the 1936 edition, but the large amount of fresh material has necessitated considerable rearrangement to secure efficient treatment. There are now eleven chapters instead of ten, and these relate to the formation of diazo compounds, their stability including its variation with pH, the relation between pH and constitution and their modes of stabilisation, their reactions, and their analytical determination—a chapter in which all the miscellaneous applications have been assembled together with the thermochemistry of the diazo compounds. The theories which have been advanced for the mechanism of the diazotisation process itself are now appropriately placed in the first chapter on methods of diazotisation, while the formation of azo compounds by coupling reactions is associated with its kinetics and mechanism. All the regrouping has greatly added to the comfort of perusal.

Most academic readers, however, will turn with anticipation to the final chapter on theories of the constitution of the diazo compounds, since the first edition had left the student with the feeling not only that the constitutional problem was left unsettled, but that a situation existed in which contrary conclusions had been urged from the same observation. Within recent years, however, the problem has been re-examined from modern viewpoints, and one might almost venture to predict that a solution is well within the possibility of achievement. In the reviewer's opinion, if the transition from the coupling product first produced by the addition of potassium cyanide to a diazonium salt to the *anti*-diazocyanide involves an intermediate *syn*-diazocyanide which slowly changes to the *anti*-isomeride, then the problem is solved.

The author himself has been fair to all the various disputants, and he has marshalled the bewildering variety of arguments in such a manner as to make an entrancing story of one of the greatest controversies in the whole of chemistry. The new volume has perhaps its greatest twin-utility in the enormous number of references, for which the author expresses the hope that no key reference has been omitted, and in the numerous experiments described with adequate detail for their performance. All the references cited are not in the text, since this would have made the work too unwieldy. Papers with good references to yet earlier literature are specially marked, but chemists are warned by the author that these lists are *not* complete, for it is impossible to include all references to diazo compounds in the literature.

The author fears that his attempt at a compromise between the needs of students and those of professional chemists has made the work less satisfactory to either, but this fear is groundless, since the book will prove a boon to both. One has only to study the comprehensive series of indexes to appreciate the last remark.

Finally, the reviewer has no hesitation in stating that the author has richly earned the gratitude of chemists for this critical and stimulating work.

H. H. HODGSON

### Fluorescence and Phosphorescence

By Peter Pringsheim. Pp. xvi + 794. New York and London: Interscience Publishers. 1949. Price, \$15.00 or 120s. 0d.

Professor Pringsheim has long been well known to workers in the field of luminescence as the author of *Fluoreszenz und Phosphoreszenz*, published in 1927. This massive new volume is a greatly enlarged and modernised form of that work. The author is an omnivorous reader of original papers, as well as a contributor on his own account, and the text is built round 1936 literature references, probably a complete list of all published work on the subject. His approach is wholly academic and closely follows the course of historical development. He is scrupulously fair to every investigator and impartial in his judgments, but does not care to sharpen the outlines of the subject by selective treatment. The phenomena fall into three distinct divisions—luminescence of gases, where the emphasis is on energy interchanges; of solutions, where quenching processes are often associated with photochemical changes; and of solids, where "luminescent centres" and "electron-traps" still remain mysterious. Dyes show effects falling particularly in the second and also in the third division. Important information concerning reactive energy levels of dye molecules is obtainable from measurements on luminescent phenomena, and this book will be invaluable to research workers seeking background knowledge. In accuracy of statement it is entirely reliable; a number of spelling and other minor errors remain for correction in a later edition.

E. J. BOWEN

### The McDougall Collection of Indian Textiles from Guatemala and Mexico

By Laura E. Start. *Pitt Rivers Museum Occasional Papers on Technology* (2). Pp. 114. Oxford University Press 1948. Price, paper, 15s. 0d.

This handbook gives a very complete account of the clothing worn by primitive natives who carry on, almost unchanged, the traditional fashions of their famous Mayan ancestors. These are relatively undisturbed by more modern influences, even with the impact of commercial yarns and "aniline" dyes. The clothes are all woven on primitive equipment or embroidered in designs based on about six colourings.

Unfortunately the actual dyeing methods are badly described and too vague for accurate record. Indigo made from indigenous *piedro de añil* is widely used for wool and cotton. Wool is saturated with an indigo infusion and salt from "the dried lake-bed", and then boiled with stannous chloride solution, which sounds quite modern. Cotton is dyed, using lime or wood ash as "mordants", but actually the description is one of a fermentation vat. Blacks are dyed with logwood, shaded with other extracts from local plants, using ferrous sulphate for mordanting; formerly a local ferruginous mud was used. The method is said to be the same as that recorded in sixteenth century Hispano-American accounts. Cochineal is dyed nowadays with stannous chloride and lime-juice, surely a modern innovation.

No printing is recorded, despite a suggestion of Indonesian influences. *Ikats*, patterns produced by *Plangi* dyeing, were held in great respect in early times, and in 1535 a large quantity were sent to the Spanish Viceroy as tributes. The art is now almost extinct; the beauty of design is secured by accurate knotting or tying of warp or weft followed by rapid dyeing in indigo, the pattern being visualised by the weaver.

The work should be of interest to designers and colourists; it is intended, of course, for anthropologists. More attention to dyeing history would have been welcome.

J. W. REIDY

### Textile Testing

#### Physical, Chemical, and Microscopical

By J. H. Skinkle. 2nd edition 1949. Pp. xii + 353. Brooklyn, N.Y.: Chemical Publishing Co. Inc. Price, \$7.75.

Professor Skinkle published the first edition of his book in 1940. The new edition is in line with those of other books on textile and textile chemical testing which have appeared lately. All these second editions show the continuing and increasing interest in laboratory control methods in this field. In the second edition now under review there has been the usual expansion, of 81 pages, partly offset by there being fewer words on the new pages. Despite this expansion, but perhaps because there has been a change of publisher, who has used thinner paper, the second edition is less bulky than the first.

A comparison of the contents of the two editions shows that the texts are generally similar. In

detail it is seen that old matter has been revised and new matter added, as in Chapter XIII, where there is a new and elaborate analytical scheme for the identification of substances used in finishing textiles. Another detailed change is that some of the tables which were collected in the appendix of the first edition have been distributed throughout the new text. Others of the original tables have been jettisoned. All the figures of the new edition are either new or have been remade. Thus all the original line diagrams which have been retained have been redrawn more neatly.

The book gives a useful survey of physical, chemical, and microscopical methods. As is natural and not inappropriate, the emphasis is on American methods, but there is, of course, the usual foundation of testing methods common to all laboratories. The information in the text is supplemented by useful bibliographies at the end of each chapter, though these were expected to be more up-to-date than they are. There is only one reference to a publication later than 1945 and that is to a paper by the author of the book. It looks as if there had been considerable delay in bringing out the new edition, a happening which is more understandable here than in the U.S.A. Because of this delay the book is not always up-to-date in reference to new developments such as the identification of new fibres. In spite of this limitation, the book will be found of value, and it can be recommended because the author has approached the subject critically and because it is the best in its field.

No serious errors were noticed, but there were a few minor ones such as the last page being numbered "953". The style is clear and understandable, but occasional words like "zeroed" will startle the English reader.

J. M. PRESTON

### Chemical Analysis

#### Volume I

### The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents

By M. B. Jacobs. 2nd revised and enlarged edition 1949. Pp. xviii + 788. New York and London: Interscience Publishers. Price, \$10.00 or 96s. 0d.

This book, first published 1941, revised and reprinted 1944, and now revised and enlarged by a further 127 pages, is Volume I of six monographs under the main title *Chemical Analysis*. Whereas the other five deal with specialised branches of analytical chemistry, intended for the specialist, this is intended by the author to be a contribution to analytical chemistry in industrial hygiene, useful in industry, insurance, education, Government regulation, research, hospitals, and for chemists, toxicologists, and physicians. In this second edition, material has been deliberately included to supply historical background to increase its usefulness for educational purposes.

The arrangement follows precisely that of the previous edition, viz. a section dealing in a general way with definitions of industrial hazards; one



dealing in detail with sampling, measurement of gas volumes, absorption, and the measurement of dust; detailed methods of estimation of harmful materials classified under metals, non-metals, and organic chemicals, subdivided into hydrocarbons, phenols, nitrogen compounds, etc.; finally, an appendix of tables giving the probable safe concentration limits of exposure for gases, vapours, and dusts.

The section on chemical warfare agents is omitted, and the remaining sections have been expanded by the addition of such historical matter as the details of the Donora "smog" disaster of 1948, and the inclusion of additional analytical methods, but not all the D.S.I.R. standard methods for the determination of toxic substances are included.

The reader of this *Journal* will regret that mention of colouring matters is still restricted to the intermediates used as fur dyes, and that textile auxiliaries, the naphthylamines, and benzidine receive no mention. Recent developments in nuclear energy have resulted in only a slight expansion of the section on radioactive substances, but the rapid developments in this and other fields of industrial activity, giving rise to new hazards, have been such as to make it impossible to deal adequately with them in a single volume surveying the whole field.

In this new edition the student will welcome the additional background material, and the specialist the lengthened lists of selected references.

G. BREARLEY

## Reports on German Industry

### I.G. Farbenindustrie A.-G., Leverkusen Dyes and Intermediates—Mothproofing Agents

FDX 682\* (PB 73,888; Microfilm N 83).  
Microfilm of many laboratory reports on work done during 1932-44 on triphenylmethane dyes, auxiliary agents, and Eulans of the BL, CN, NK, and SN types. Information is given on work on many intermediates, dyes, and mothproofing agents which had not reached the commercial production stage. C. O. C.

### I.G. Farbenindustrie A.-G., Leverkusen Dyes, Intermediates, Textile Auxiliaries, Chlorinated Rubber, Plasticisers, Driers, Wetting Agents, Mothproofing Agents

FDX 676\* (PB 73,754; Microfilm L 85).  
Microfilm of a large number of reports, in German and dated 1936-38, dealing with research work on dyes and intermediates, mothproofing compounds, auxiliary agents, etc. C. O. C.

### I.G. Farbenindustrie A.-G., Ludwigshafen, Hoechst, Leverkusen, Uerdingen, and Wolfen Manufacturing Directions for Dye Intermediates and Textile Auxiliaries

FDX 622\* (PB 74,239; Microfilm D 10).  
Microfilm of many manufacturing directions, in German, for intermediates for dyes and auxiliary agents as well as for the following—

Ampho Soap DN, SS, and 18  
Cyclanone BN, F, L, LA, LK, LOK, O, OA, OAM, WN,  
WNL, and WNM  
Emulphor FM  
Eunaphtol AS and ASOT  
Fur Scouring Agent LM, TA, and TAV  
Laventine BL, HW, HWM, and KB  
Lenocal AL and C  
Leonil S and SBS  
Leophen B, BE, and BN  
Ludorit  
Luwa  
Mollescal BM and C  
Monopol Brilliant Oil SO 100%  
Nekal A, BX, BXG, BXS, S, and solution FES  
Nuva LA and OL  
Peregal OK  
Persistol N, NA, and WE  
Ramasit I, III, BK, FP, K, KG, KGM, KGT, KJ, KT,  
KW, WD, and ZN  
Soromin A, AF, CR, FL, and SG  
Wetting Agent SL  
Trilon A

In addition instructions for the manufacture of various Eukanols are given. C. O. C.

### I.G. Farbenindustrie A.-G., Offenbach Manufacture of Various Chemicals and Dyes Tests of Dyes for Fastness

FDX 635\* (PB 70,428; Microfilm E 25).  
A microfilm of a large number of research reports and manufacturing instructions for various organic chemicals and dyes. There are several tables of fastness properties of dyes. There is a long paper (35 pp.) on the Aldazines of Aromatic Hydroxyaldehydes as regards their Fluorescent Properties, another (14 pp.) on Benzo Fast Chrome Blues, and another (10 pp.) on the Structure and Properties of Neutral-dyeing Dyes for Perlon. C. O. C.

### Reichsforschungsrat und Reichsamt für Wirtschaftsausbau, Berlin Research Reports on Synthetic Fibres 1939-45

FDX 660\* (PB 73,601; Microfilm B 215).  
Microfilm of a large number of research reports, in German, from rayon manufacturers and makers of auxiliary agents for use with rayon. C. O. C.

### Degussa, Frankfurt Bleaching with Hydrogen Peroxide and Sodium Chlorite—Carbon Black

FDX 642\* (PB 74,423; Microfilm G 289).  
Microfilm of numerous miscellaneous reports, in German, many of which deal with various aspects of the use of hydrogen peroxide and sodium chlorite in bleaching. Others deal with the production of Carbon Blacks. C. O. C.

### Deutsche Gold- und Silberscheideanstalt Hydrogen Peroxide, Washing and Bleaching of Cellulose Hydrate, Ripening of Viscose, Use of Rare Earths in Textile Finishing

FDX 659\* (PB 74,421; Microfilm G 291).  
Microfilm of a large number of laboratory and works reports, including several on the use of hydrogen peroxide in the bleaching of cellulosic products and the ripening of viscose. A report on the use of rare earths says that neither cerium nor thorium has any advantage for peroxide bleaching, as they are both less efficient stabilisers than magnesium. Thorium compounds are superior to cerium compounds as delustrants for rayon. C. O. C.

### I.G. Farbenindustrie A.-G., Ludwigshafen Methods of Analysis

FDX 655\* (PB 70,065; Microfilm G 25).  
A microfilm, in German, of 72 methods of analysis developed in various I.G. laboratories. C. O. C.

\* Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, 40 Cadogan Square, London S.W.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.



# Abstracts from British and Foreign Journals and Patents

(The Titles of Patents are abridged and modified)

## I—PLANT; MACHINERY; BUILDINGS

### Solving Corrosion Problems in the Textile Industry.

R. B. Seymour and W. L. Worth, Jr. *Amer. Dyestuff Rep.*, 38, 735-737 (3rd Oct. 1949).

Methods of overcoming the following problems are suggested—protection of floors from attack by acid or alkali, construction of vessels used for bleaching and dyeing, disposal of wet-processing liquors, and counteraction of corrosion in equipment used for manufacturing viscose rayon. A. S. F.

### Mechanisation of Screen Printing. J. Sieger. *Melliand Textilber.*, 29, 351-352 (Oct. 1948).

A review is given of the developments in the mechanisation of screen printing which have led up to the production of the Karussell rotary flat printing machine. In this machine the screens are disposed around a horizontal disk, and the change of colours for each repeat is effected by one rotation of the disk. F. A.

## PATENTS

### Yarn-impregnating Machine. E. J. Heizer and Specialties Development Corpn. U.S.P. 2,476,298.

The yarn is fed on to a roll which is in contact with two other rolls so as to make entering and leaving nips. These two rolls reciprocate longitudinally along their axes, thus repeatedly untwisting and retwisting the yarn during its passage over the first roll. This facilitates impregnation of the yarn by liquor supplied to any of the rolls. C. O. C.

### Control Switch for Selvage Guides, etc. of Tenters, Printing Machines, etc. J. Dugler. B.P. 630,717.

A driving member is rotated by the moving fabric and is engaged with a rotatable driven member. The driven member has a switch mounted on it whose contacts are operable when the driven member is rotated to close the circuit of the selvage guide, etc. and open it when the driven member is stationary. C. O. C.

### Tension Control for Running Webs. Cameron Machine Co. B.P. 630,995.

Roller Printing Machines. E. Rebuffa and A. Ciprandi. B.P. 630,880.

A multicolour machine is described which uses no back greys, the fabric passing directly between the pressure and printing rollers. Excess colour is continuously removed from each printing roller, and each pressure roller is continuously cleansed, washed, and dried. C. O. C.

### Doctor Mechanism for Rolls and Cylinders. E. R. Ljungquist and Loddig Engineering Corpn. U.S.P. 2,477,339.

The holder for the doctor blade is so constructed that while the blade is applied, as a whole, to the roll by turning of the holder, auxiliary pressure can be applied in varying amounts to localised areas of the free or back edge of the blade to cause the blade to fit itself closely to the surface being doctored. C. O. C.

### Screen Printing Apparatus. D. Walker and David Evans & Co. Ltd. B.P. 631,135.

Screen Printing Bottles, Jars, Panels, etc. British Hartford-Fairmont Syndicate Ltd. B.P. 631,496.

A machine is described which automatically prints simultaneously the opposite sides of a panel or the four sides of a square bottle, etc. C. O. C.

### Felt-hardening Machines. William Bywater Ltd. and C. I. Leather. B.P. 630,849.

The thickness of the felt is more efficiently controlled if the hardening machine has a fixed bottom plate and an adjustable top plate. The top plate has a fixed stop at each corner which can be engaged by an adjustable stop mounted on a fixed part of the machine, thus enabling the setting of any required final or minimum distances between the plates. C. O. C.

### Fur-carrotting Machine. W. L. Braun and Carrotting Machine & Chemicals Co. Inc. U.S.P. 2,479,466.

Hat-felt Hardening Machine. H. M. Goodechild and Merrimac Hat Corpn. U.S.P. 2,479,228.

### Rotatable Drum-type Machine for Treating Materials with Liquids. E. G. Wilson. B.P. 631,048.

### Dry Cleaners' Spotting Machine. Bill Glover Inc. B.P. 631,564.

Either steam or hot air is supplied at will to the nozzle of the machine. C. O. C.

### Impregnating Paper. W. E. Holland, A. J. Stanley, J. A. Chesnut, and Industrial Tape Corpn. U.S.P. 2,477,604.

Paper is rapidly impregnated by using a series of at least three rollers each partly immersed in the treating liquor. The paper passes over the first and third rollers and under the second roller. The liquor is thus applied to one side of the paper before the other, preventing air bubbles from being entrapped in the paper. C. O. C.

### Impregnating Articles formed of Paper or other Fibrous Material. R. H. von Liedtke and Line Material Co. U.S.P. 2,478,439.

Fur-conditioning Machine. S. Friedman and Reliable Machine Works Inc. U.S.P. 2,477,448.

A machine is described which is particularly suitable for brushing and ironing finished fur garments, including those which are considerably larger than the conditioning drum. The fur body is caused to contact a substantial area of the conditioning drum, undesired strains on the fur being at the same time minimised. The pressure of the fur against the drum can be closely controlled, thus enabling the machine to be used for varying types of fur or for furs of the same type in varying conditions of wear. C. O. C.

## III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

### Linamarin and its Enzyme Linamarase. G. H. Veltman. *Melliand Textilber.*, 29, 310-312 (Sept. 1948).

The literature on chemical and physiological investigations concerned with linamarin is reviewed with 63 references. F. A.

### Chlorites in the Textile Industry. J. Meybeck. *Teintex*, 14, 505-519 (Dec. 1949).

The literature is reviewed dealing with the preparation of chlorites, the stability of aqueous solutions of chlorites under various pH conditions, the reaction between chlorites and hypochlorites, chlorine, hydrogen peroxide, and aldehydes. A tabular synopsis is given indicating the resistance to chlorites of a range of non-ferrous metals and alloys and plastic materials used in the construction of vessels used in wet processing of textiles, and also of resins, etc. used for coating the insides of such vessels. The industrial application of chlorites in bleaching cotton, cellulose rayons, bast fibres, silk, wool, and synthetic fibres is discussed. B. K.

### Application of a Theory of Catalysis by Molecules of Permanent Electric Moment to Drying Oil Chemistry. R. Jacquemain and J. Berger. *Congr. tech. intern. Ind. Peintures Ind. assoc.*, 1, 454-456 (1947); *Chem. Abs.*, 43, 8694 (10th Nov. 1949).

In an elaboration of the theory that the oxidation of unsaturated organic compounds is catalysed by a polar body it is suggested that the oxidation product of a drying oil is the polar body catalysing the air-drying of that oil (which mainly produces C-C-linked polymers). Its absence explains the existence of an induction period in drying. The function of metallic driers is to supply polar bodies, e.g. the Co abietate-abietic acid complex. This also explains why blown oils dry faster. Just as too much drier slows drying, too much oxidation product, together with a falling supply of unsaturated oil, brings about the fall in drying rate occurring after a maximum has been reached. C. O. C.

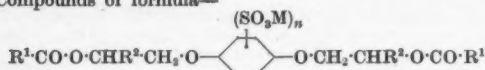
## PATENTS

### Water-in-oil Emulsions. D. X. Klein and Du Pont. U.S.P. 2,476,308.

The polymers of long-chain alkylsiliconic acids, pre-formed or formed *in situ* by hydrolysis of an alkylsilicon triester, e.g. octadecylsilicon trichloride, are dispersing agents which yield stable water-in-oil emulsions. C. O. C.

**Aliphatic Esters of Nuclear-sulphonated Quinol Bishydroxyalkyl Ethers.** J. R. Caldwell and Eastman Kodak Co. U.S.P. 2,478,368.

Compounds of formula—



(M = H, alkali metal, or HAM (Am = a non-aromatic amine);  $n = 1$  or  $2$ ;  $R^1 = C_8\text{--}C_{20}$  alkyl or cycloalkyl;  $R^2 = H$  or  $CH_3$ ) have surface-active properties, are valuable emulsifying agents for the preparation of emulsions for treating textiles, and are effective wetting and levelling agents in dyeing, scouring, and finishing processes. C. O. C.

**Soluble Starches.** H. R. Blattmann, A. H. Blattmann, M. H. Tesdorpf, and Blattmann & Co. B.P. 630,914.

Soluble starches and dextrans of improved colour and homogeneity are made by impregnating starch with an acidic starch degradation agent, e.g. HCl, and heating to 80–90°C. under vacuum until the moisture content is 10%. Degradation is completed by further heating to 165°C. either *in vacuo* or in an inert atmosphere. J. W. B.

**Starch Derivatives.** National Starch Products Inc.

B.P. 631,242.

Ungelatinised starch derivatives which give clear solutions are prepared by reaction of ungelatinised starch and water with a carboxylic acid anhydride under alkaline conditions. J. W. B.

**Carboxyalkyl Ethers of Carbohydrate Gums.** O. A. Moe and General Mills Inc. U.S.P. 2,477,544.

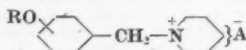
The carboxyalkyl ethers of locust-bean and other carbohydrate gums are readily dispersible in water and form sols of excellent clarity as compared with the untreated gum. The viscosity of the solutions is never less than that of the untreated gum and in some cases is increased somewhat. The solutions gel if a dilute solution of a metal salt, e.g. FeSO<sub>4</sub>, is added, the gels being very firm and transferable from one vessel to another without wetting the surface. They can be formed by treating the gum with cold aqueous sodium hydroxide and then with a halogenated fatty acid. C. O. C.

**Alkaline Washing Agents.** Société des Produits Peroxydes. B.P. 630,864.

Washing agents containing active oxygen consist of a hydrated mixture which comprises chiefly the following components—(a) sodium percarbonate mixed with a stabiliser, e.g. magnesium silicate, (b) sodium silicate, (c) one or more sodium salts with an alkaline reaction and capable of forming a hydrate, and (d) optionally soap, the agent containing 30–35% of water by weight of dry silicate in addition to that required by the hydrated sodium salt. J. W. B.

**Alkoxybenzylpyridinium Compounds—Antiseptic Detergents.** G. A. Alles and B. B. Wisegarver. U.S.P. 2,477,850.

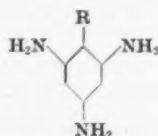
Compounds of general formula—



(R = C<sub>12</sub>–C<sub>18</sub> alkyl, A = an anion), e.g. 2-dodecyloxybenzylpyridinium chloride, have excellent antiseptic properties even in strongly alkaline solutions and are active cationic detergents. C. O. C.

**Monocyclic Aromatic Triisocyanates and Related Compounds—Textile and Rubber Auxiliary Agents.** J. Munro, E. Gill, and I.C.I. Ltd. B.P. 631,007.

A compound (1 mol.) of general formula—



(R = H, Alk, Alk-O, or Ar-O) is treated with not < 1.5 mol. of phosgene in a volatile organic solvent, and the product heated to not > 90°C. while phosgene is passed

through the suspension and hydrogen chloride removed from it.

B.P. 631,025.

Phosgene is passed into a suspension of a compound of the above general formula maintained at 90–130°C. while the hydrogen chloride liberated is removed. C. O. C.

**Hydroxymethylbehenamide and Related Compounds—Intermediates for Water-repellent Agents.** J. Pikl and Du Pont. U.S.P. 2,477,346.

Compounds of general formula R-CO-NH-CH<sub>2</sub>OH (R = C<sub>21</sub>H<sub>43</sub> or C<sub>22</sub>H<sub>45</sub>O), e.g. N-hydroxymethylbehenamide or docosyl N-hydroxymethylcarbamate, are intermediates for agents which impart a water-repellent finish of outstanding fastness to washing and dry cleaning. Thus the above amide converted into behenamidomethylpyridinium chloride and applied as a 1% solution to cotton cloth in the standard manner gives as good a water-repellent finish as a 3% solution of stearamidomethylpyridinium chloride, and the finish is much more resistant to repeated washing and dry cleaning. C. O. C.

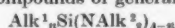
**Water-soluble Esters of Alkylsiliconic Acids.** D. X. Klein, D. E. Kvalnes, and Du Pont.

U.S.P. 2,476,307.

Surface-active, hydrolysable, water-soluble esters of alkyltrihydroxysilanes are obtained by treating 1 mol. of a compound of general formula R-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (R = alkyl of > 11 C) with 3 mol. of a polyethylene glycol having a chain of 2–12 -O-CH<sub>2</sub>-CH<sub>2</sub>- units. They are useful dispersing agents, and when applied to textile fibres and then heated to 100–150°C. impart a water-repellent finish. C. O. C.

**Organosilylamines—Waterproofing Agents.** Corning Glass Works and O. K. Johannson. B.P. 629,483.

Organosilicon compounds of general formula—



( $n = 1$  or  $2$ ) are useful waterproofing agents, and have the advantage over organosilicon halides that upon hydrolysis they yield dialkylamines and neutral silicones and so have less tendency to cause tendering of cellulosic textiles. They are readily produced by treating an organosilicon halide with a dialkylamine under anhydrous conditions. C. O. C.

**Wrinkle Coating Composition consisting of a Mixture of Conjugate-double-bonded Oil and an Aqueous Emulsion of Polyvinyl Acetate Resin.** N. T. Beynon and New Wrinkle Inc. U.S.P. 2,479,298.

**Polyallyl Ether Compositions containing an Orthosilicate Ester.** J. R. Roach and General Mills Inc. U.S.P. 2,477,548.

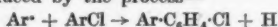
Heat-curable compositions, useful for impregnating cloth or paper, as surface coatings, or for moulding, comprise a polyallyl ether of a polyhydric alcohol and not < 10% on the weight of the ether of a non-volatile saturated ester of orthosilicic acid. The cured compositions are insoluble and infusible and have excellent resistance to wear, chemical attack, water, and fire. C. O. C.

## IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

**Kinetics and Mechanism of the Sandmeyer Reaction.** W. A. Cowdrey and D. S. Davies. J.C.S., Supplementary Issue No. 1, S 48–S 59 (1949).

The kinetics of the Sandmeyer reaction for replacing diazonium groups by halogen has been investigated. The reaction is of the first order with respect to both diazonium ion and dissolved cuprous chloride: the rate is, however, inversely proportional to the square of the total chloride ion concentration. From the results at ~0°C. and in dilute solution, it is inferred that the primary reaction involves collision between ArN<sub>2</sub><sup>+</sup> and CuCl<sub>2</sub><sup>-</sup> ions, and that the latter are converted into (unreactive) CuCl<sub>3</sub><sup>2-</sup> ions at higher chloride concentrations. The rate of the Sandmeyer reaction of substituted diazonium compounds decreases in the order  $p\text{-NO}_2 > p\text{-Cl} > H > p\text{-CH}_3 > o\text{-CH}_3 > p\text{-OCH}_3$ . The symmetrical azo compound is the major by-product: its yield increases with the CuCl<sub>2</sub><sup>-</sup> concentration, and in certain circumstances it is formed as a complex with cuprous chloride. Minor by-products include the hydrocarbon ArH, the phenol ArOH, in one case the diaryl Ar-Ar, and an unidentified water-soluble

fraction. The suggested mechanism, which involves only simple binary collisions, is—(a) slow co-ordination of the terminal nitrogen atom of  $\text{ArN}_2^+$  to the copper in  $\text{CuCl}_2^-$ , giving  $[\text{ArN}_2\text{CuCl}_2]$ ; (b) decomposition of this to  $\text{ArCl}$ ; or (c) further fast addition to it of  $\text{ArN}_2^+$  to give  $[(\text{ArN}_2)_2\text{CuCl}_2]^+$ , which either (d) decomposes to  $\text{ArCl}$  or (e) reacts with  $\text{CuCl}_2^-$  to give  $\text{Ar}\cdot\text{N}:\text{N}\cdot\text{Ar}$ . The main objections to a free-radical mechanism for the Sandmeyer reaction with cuprous chloride are stated by the present authors to be—(a) absence of extensive reactions between  $\text{Ar}\cdot$  radicals and water molecules to yield large percentages of phenol  $\text{ArOH}$  and/or hydrocarbon  $\text{ArH}$ ; (b) absence of unsymmetrical diaryls produced by the process—



(c) the fact that an increase in diazonium concentration, which would increase the probability of interaction between  $\text{Ar}\cdot$  and  $\text{ArN}_2^+$ , does not increase the yield of azo compound over most of the  $[\text{ArN}_2^+]$  range. Again, the Sandmeyer reaction leads to identical yields whether diazonium chloride or sulphate is used; this necessitates the assumption that in a solution containing more  $\text{Cl}^-$  than  $\text{CN}^-$  the radical always reacts with  $\text{CN}^-$ , although in other circumstances a reaction with  $\text{Cl}^-$  must be postulated.

H. H. H.

**Azo Dyes from Sulpha Drugs.** T. R. Ingle, N. V. Brangi, N. L. Phalnikar, and B. V. Bhide. *J. Univ. Bombay*, **17A**, (5), 72-75 (1949); *Chem. Abs.*, **43**, 9047 (25th Nov. 1949).

Azo dyes prepared by condensing phenols with diazotised  $p\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$  or its analogues in some cases are more effective than the parent sulpha drug against some species of bacteria, and in other cases or against other bacteria they are less effective.

C. O. C.

**Studies in Coal-tar Colours, FD&C Yellow No. 6 and C.I. No. 26.** C. Stein. *J. Assocn. Offic. Agr. Chemists*, **32**, 672-679 (1949); *Chem. Abs.*, **43**, 9451 (25th Nov. 1949).

A sample of pure FD&C Yellow No. 6 (Sunset Yellow), disodium salt of 1-*p*-sulphophenylazo-2-hydroxynaphthalene-6-sulphonic acid (I), was required for checking the validity and accuracy of normal methods of examination of this dye for its compliance with U.S. food laws. As the sodium salt of 1-phenylazo-2-hydroxynaphthalene-6-sulphonic acid (II) (C.I. 26) is a possible impurity in commercial I, a pure sample of II was made to aid in developing a method for subsidiary dyes in I. Diazotised sulphanilic acid was coupled with 2-hydroxynaphthalene-6-sulphonic acid, and the resulting dye (I) separated and purified. II was made by coupling diazotised aniline with 2-hydroxynaphthalene-6-sulphonic acid. Elementary analyses and  $\text{TiCl}_3$  titrations showed that I was 99% and II > 98% pure. II can be differentiated from I spectrophotometrically by its secondary peak at 410 m $\mu$ , in neutral solution, or more readily by its curve in alkaline solution. The A.O.A.C. procedure (*Methods of Analysis A.O.A.C.* (6th edition 1945), p. 293) for subsidiary dyes in I will determine II.

C. O. C.

**Diazophenanthrene Series—Cation-halochromy of Quinoline and Diazophenanthrene Derivatives.** G. Bargellini. *Atti Accad. Lincei, Classe sci. fis., mat., e nat.*, **5**, 50-55 (1949); *Chem. Abs.*, **43**, 9376 (25th Nov. 1949).

The effect of substitution groups on colour is noted for a large number of quinoline and diazophenanthrene derivatives.

C. O. C.

**Spectrophotometric Study of Three Zirconium Lakes.** J. F. Flagg, H. A. Liebhaufsky, and E. H. Winslow. *J. Amer. Chem. Soc.*, **71**, 3630-3632 (Nov. 1949).

Zirconium forms definite compounds with Alizarin, Purpurin, and Quinalizarin, the two constituents being combined in equimol. amounts. The three lakes probably have a chelate-ring structure analogous to that of the hafnium-alizarin lake.

C. O. C.

**Synthesis of Infrared-sensitive Dyes. XV—Nonamethinecyanines.** T. Ogata and T. Isa. *Bull. Inst. Phys. Chem. Research* (Tokyo), **21**, 860-864 (1942).

**Chemistry of Melanin. V—Oxidation of Dihydroxyphenylalanine by Tyrosinase.** H. S. Mason and C. I. Wright. *J. Biol. Chem.*, **180**, 235-247 (1949).

**Crystalline Characteristics of Four Carotene Isomers.** F. T. Jones and E. M. Bickoff. *J. Assocn. Offic. Agr. Chemists*, **31**, 776-781 (1948); *Chem. Abs.*, **43**, 6881 (25th Sept. 1949).

Four isomers were prepared from a commercial carotene by chromatographic adsorption. *all-trans-β*-Carotene (I) is platy and tends to cluster. The plates are thin enough to show interference colours, six-sided, and 2-4 times as long as wide. The nearly perfect ones had a terminal angle of 75°. Refractive index > 1.68. *all-trans-α*-Carotene (II) crystals resemble those of I. Terminations are more nearly perfect. *neo-β*-Carotene U crystals differ from I and II, being tapering needles or narrow blades tending to cluster. In polarised light the extinction is parallel. Refractive index < 1.68. *neo-β*-Carotene B crystals grow only in spherulitic aggregates. There are six photomicrographs.

C. O. C.

**Colour in Mexican Life [Aztec Dyes and Pigments].** P. Westheim. *Ciba Review*, (70), 2576-2580 (Sept. 1948).

Animal, vegetable, and mineral pigments were in use by the Aztecs, by far the most important being cochineal, the use of which was spread to Europe by the Spaniards. A gum-like resin pressed from the seeds of *Salvia chian*, used by the Aztecs, is still in use to-day, under the name of Xixi or Chichi, as a fixing agent both for dyes and in paints.

C. O. C.

**Meratin—Yellow Colouring Matter in the Flower of *Meratia praecox*.** K. Hayashi and K. Ōuchi. *Acta Phytochim.* (Japan), **15**, 1-8 (1949); *Chem. Abs.*, **71**, 8449 (10th Nov. 1949).

Meratin is 3-*O*-diglucoisidylquercetin.

C. O. C.

**Yellow Dye from the Kariyasu Plant, *Anthraxon hispidus*.** K. Hayashi and T. Inoue. *Acta Phytochim.* (Japan), **15**, 53-58 (1949); *Chem. Abs.*, **71**, 8450 (10th Nov. 1949).

The yellow dye obtained from the dried plant is a luteolin monocarabinoiside.

C. O. C.

**Channel and Furnace Carbon Blacks.** G. J. Duffy. *Official Digest Federation Paint & Varnish Production Clubs*, (293), 347-352 (1949); *Chem. Abs.*, **43**, 8647 (10th Nov. 1949).

Following a review of the manufacturing conditions influencing the quality of channel black it is stated that the pigment normally produced by partly burning a natural gas and collecting in cool iron channels contains approx. 5% of chemically bound gas, largely oxygen and hydrogen. These gases improve wetting properties, stabilise dispersions, and reduce affinity for drier metals. Carbon black made by cracking natural gas and collecting the pigment in a large flue has a larger particle size than channel black, contains no chemically bound gas, and has pH approx. 9.0 compared with 2.5-5.5 for channel black. Furnace blacks made from liquid hydrocarbons are a cross between lampblack and carbon black and are finding favour because of their economy as compared with true lampblacks.

C. O. C.

**Coloration of Glass by Gold, Silver, and Copper.** S. D. Stookey. *J. Amer. Ceram. Soc.*, **32**, 246-249 (1949); *Chem. Abs.*, **43**, 8111 (1949).

These metals dissolve in molten glass in an oxidised state, not as free metal. The glass remains colourless as long as the metal is oxidised. When reducing conditions are produced, the free metal is formed and the characteristic colour appears. In absence of a reducing agent, glasses can be cooled to room temperature and reheated and still retain the metal in an ionic state, the glass remaining colourless. These metal ions are susceptible to photochemical reduction.

C. O. C.

**Zinc Yellow.** M. Pratz. *Chim. Peintures*, **12**, 201-205 (1949); *Chem. Abs.*, **43**, 8697 (10th Nov. 1949).

Zinc yellow was prepared by adding a dil. solution of  $x$  mol.  $\text{H}_2\text{SO}_4$  to a slurry of 1 mol.  $\text{ZnO}$ , and then adding an aqueous solution of  $y$  mol.  $\text{K}_2\text{Cr}_2\text{O}_7$ . Maximum yields were obtained at  $x = 0.25$  for any value of  $y$ . The precipitate was  $3\text{ZnO}\cdot\text{ZnSO}_4\cdot 4\text{H}_2\text{O}$  when  $y = 0$ ; the solution always contained  $\text{ZnSO}_4$ . If  $x = 0.25$ , the yield was maximum for  $y$  not < 0.5; excess  $\text{K}_2\text{Cr}_2\text{O}_7$  was always present. The precipitate was  $4\text{ZnO}\cdot 4\text{CrO}_3\cdot \text{K}_2\text{O}\cdot 3\text{H}_2\text{O}$  when  $y > 0.5$ .

C. O. C.



**Zinc Chromate Primers.** H. B. Kirkpatrick. *Australia Dept. Supply & Development, Paint Notes*, 4, 174-183 (1949); *Chem. Abs.*, 43, 8697 (10th Nov. 1949).

Sulphate- and chloride-free zinc yellow  $4\text{ZnO} \cdot 4\text{CrO}_3 \cdot \text{K}_2\text{O} \cdot 3\text{H}_2\text{O}$  in a sufficiently water-permeable vehicle (high phthalic-linseed oil-alkyd is recommended) is an excellent rust-resisting primer for low-C steel. Rust retardation is probably due to slight solubility of the zinc yellow.

C. O. C.

**Crystal Form and Paint-technical Properties of Chrome Green.** C. R. Broekers. *Verfkronek*, 22, 99-103 (1949); *Chem. Abs.*, 43, 7237 (1949).

The most important component of chrome green is chrome yellow. Precipitation of the latter gives first microscopically small, rhombic crystals, which soon coalesce to form monoclinic crystals. The velocity of this transformation depends greatly upon the acid residue with which the lead is combined, organic acids giving slower transformation than inorganic. This change in crystal form can be noticed also by change in hue. The monoclinic modification is darker, the degree of darkening depending on the  $\text{PbCrO}_4 : \text{PbSO}_4$  ratio. The transition temperature, i.e. that at which the first monoclinic crystals are formed, can be determined very accurately by microscopic examination. It rises with increasing  $\text{PbSO}_4$  ratio to about  $40^\circ\text{C}$ , when no more transformation occurs. The rhombic chrome yellow crystals are not very fast to light, and have little covering and colouring power and high sedimentation; the monoclinic crystals are fast to light, and have better covering and colouring power and little sedimentation. These properties, which are favourable for lake manufacture, improve with increasing length of the crystals, but if the latter grow too large they cause dichroism or streaking. Water-soluble lead salts are used to precipitate the chrome yellow, as they give the most favourable crystal growth, i.e. monoclinic but not too long; this reduces dichroism to a minimum. The second important component of chrome green is ferrocyanide blue. Its hue depends upon the amount of chemically bound water, which in turn depends upon the concentration and temperature used for precipitation. This water content increases with depth of hue and can be 10% of the pigment. Ferrocyanide blue consists of very small amorphous particles. The nature of the vehicle used when mixing the yellow and blue and the way the pigment is wetted have great influence on the paint-technical properties of the chrome green.

C. O. C.

## PATENTS

**Non-dusting Stabilised Diazo Compounds.** H. A. Bergstrom and General Aniline & Film Corp.

U.S.P. 2,477,165.

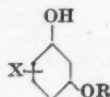
A powdered salt of a diazo compound is mixed with not < 0.5% by weight of a liquid dialkyl carbonate of  $> 4\text{C}$  but not so much that would result in liquid separation by drainage. Thus 50 parts by weight of the zinc chloride double salt of diazotised 5-nitro-*o*-anisidine or of the dye obtained by coupling diazotised *p*-nitroaniline with dihydroxyethyl-*m*-toluidine when milled with 1 part of diethyl carbonate yields a non-dusting powder of excellent stability on storing.

C. O. C.

**Resorcinol Monoesters as Diazotype Coupling Components.** General Aniline & Film Corp., W. H. von Glann, and L. N. Stanley.

B.P. 631,896.

Compounds of formula—



(R = acyl or contains sulphonyl linked to the O; X = halogen, alkyl, hydroxyalkyl, aryl, alkaryl, aralkyl, cycloalkyl, alkoxy, carboxy, or  $-\text{CH}_2\text{N}(\text{Y})_2$  (Y = the same or different, hydrogen, alkyl, hydroxyalkyl, aryl, alkaryl, aralkyl, or cycloalkyl)) coupled with diazo compounds yield deep sepia images and have good stability to precoupling.

C. O. C.

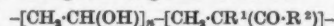
**Cyanine Dye Intermediates containing an Aryloxy-alkyl, Arylthioalkyl, or Arylselonoalkyl Group attached to the Nitrogen Atom.** General Aniline & Film Corp. and A. W. Anish.

B.P. 631,124.

**Polymeric Colour Formers resulting from Condensation of Hydroxyl Polymers containing Reactive Ketalone Groups with Reactive Methylene and Amino Colour Formers.** D. M. McQueen and Du Pont.

U.S.P. 2,477,462.

Colour formers are obtained by condensing a polymeric ketalone having recurring units of formula—



( $n = 10-50$ ,  $\text{R}^1$  and  $\text{R}^2 = \text{H}$  or hydrocarbon radicals) with acrylacetylides, acylacetic esters, cyanoacetic esters, cyanoacetamides, pyrazolones, aminopyrazolones, and aminoacetylides with elimination of water. They are useful in colour photography and in the process of U.S.P. 2,371,052 by being added e.g. to a viscose spinning solution, the fibres spun from it being treated with a diazotised aromatic amine to yield dyed fibres of outstanding fastness to laundering.

C. O. C.

**5-Acyloxypyrazoles—Dye Intermediates.** E. L. Martin and Du Pont.

B.P. 631,269.

U.S.P. 2,476,987.

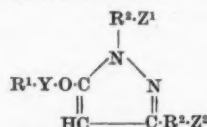
5-Acyloxypyrazoles unsubstituted in the 4 position and containing an amidoaldehyde group in at least one of the positions 1 and 3 in the pyrazole ring, and also their acetals with alkanols of 1-4 C and 1:2- and 1:3-dihydroxyalkanes of 2-4 C free from amidoaldehyde-reactive groups, are useful dye intermediates, giving red or yellow dyes when coupled with diazo compounds and blue, red, or magenta dyes when coupled with oxidised *p*-phenylenediamine.

C. O. C.

**Acid Halides of 5-Acyloxypyrazoles—Dye Intermediates.** E. L. Martin and Du Pont.

U.S.P. 2,476,986.

Compounds of general formula—



(Y = carbonyl or sulphonyl;  $\text{R}^1\text{Y}$  = an acyl radical free from acid halide-reactive groups;  $\text{R}^2$  = a bivalent organic radical linked by hydrocarbon carbon atoms to  $\text{Z}^1$  and  $\text{Z}^2$  and the cyclic N and C;  $\text{Z}^1$  and  $\text{Z}^2 = \text{H}$ , carbonyl halide, or sulphonyl halide radicals, at least one of them being an acyl halide radical), e.g. the K salt of 1-*p*-chlorosulphophenyl-3-methyl-5-pyrazolyl benzoate, couple with diazonium salts to yield azo dyes suitable for textiles. They are also useful as photographic colour formers.

C. O. C.

**5-Acyloxypyrazoleamidoacetals.** E. L. Martin and Du Pont.

U.S.P. 2,476,988.

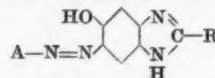
5-Acyloxypyrazoleamidoaldehyde acetals of vinyl alcohol polymers are useful dye intermediates, particularly for adding to spinning solutions for artificial fibres, the fibres formed then being treated with diazonium salts, oxidised *p*-phenylenediamine, etc. They are also useful as photographic colour formers.

C. O. C.

**Metallisable Benzimidazole Azo Dyes.** C. E. Lewis and American Cyanamid Co.

U.S.P. 2,475,506.

5-Hydroxybenzimidazoles, prepared by reduction and cyclisation of phenyl esters of 3-nitro-4-acylaminoaryl-carboxylic acids, when coupled with suitable diazo compounds give azo dyes of general formula—



(R = H, aryl, or low-carbon alkyl; A is the residue of a diazotised amine having a lake-forming group *ortho* to the azo group). Thus by coupling diazotised 4-nitro-2-aminophenol with 2-methyl-5-hydroxybenzimidazole under alkaline conditions a brown, chromable, wool dye is produced.

E. S.

**Substantive, Metallisable Polyazo Dyes.** Ciba Ltd.

B.P. 630,452.

Polyazo dyes free from sulpho groups are made by coupling two mol. of the same or different diazo compounds





### Carotene Compositions and Solutions. M. L. Hartmann and H. M. Barnett. U.S.P. 2,477,928.

Readily soluble carotene compositions, in which the carotene does not oxidise rapidly on storage nor tend to form large crystals, are obtained by grinding the carotene until the mean particle diameter is  $< 10 \mu$ , simultaneously or subsequently pasting it in an oil which is liquid at the temperature of forming the suspension, and then cooling until the paste becomes solid. C. O. C.

### Rutile Titanium Dioxide. W. J. Cauwenberg, H. L. Sanders, and American Cyanamid Co. U.S.P. 2,477,559.

Titanium sulphate is hydrolysed in presence of a hydrated titanium dioxide seeding agent having rutile crystal form or which exhibits such form upon calcining at not  $> 1000^\circ\text{C}$ . C. O. C.

### Luminescent Materials. Philips Lamps Ltd. and S. Rothschild. B.P. 628,308.

Alkaline-earth metal arsenates activated with manganese arsenate and/or antimony phosphate or arsenate display a wide range of coloured luminescence (red-blue) when subject to ultra-violet radiation. C. O. C.

### Alkaline-earth Metal Sulphide Phosphorescent Pigment. F. Stern. U.S.P. 2,475,437.

A mixture of calcium and/or strontium sulphide with a minute amount of a bismuth salt and a copper salt (0.005–0.028% Bi and 0.0005–0.007% Cu by weight of the mixture), heated at  $900$ – $1300^\circ\text{C}$ . long enough to effect diffusion of the Bi and Cu throughout the pigment, gives an increase in phosphorescent brightness of 100–200% for 30 min.–8 hr. after excitation. C. O. C.

### Blue to Bluish-green Quick-drying Writing Inks—Copper Phthalocyanine Derivatives Soluble in Aqueous Alkali. R. L. Mayhew and General Aniline & Film Corpn. (V, below.)

## V—PAINTS; ENAMELS; INKS

### PATENTS

### Blue to Bluish-green Quick-drying Writing Inks—Copper Phthalocyanine Derivatives Soluble in Aqueous Alkali. R. L. Mayhew and General Aniline & Film Corpn. U.S.P. 2,476,991.

An aqueous solution of a copper phthalocyanine having attached to the phenylene nuclei several pyridylsulphamyl or morpholinylsulphamyl groups, a hygroscopic polyhydric alcohol, and 0.5–2.0% (on the total weight of the solution) of sodium hydroxide are used. The soluble copper phthalocyanine derivatives used may be prepared by treating a copper phthalocyaninepolysulphonyl chloride with e.g. 2-, 3-, or 4-aminopyridine, morpholine, 1-*o*-aminophenyl-3-methyl-5-pyrazolone, etc. at room temperature in a suitable diluent. C. O. C.

### Zinc Chromate Primers. H. B. Kirkpatrick. (IV, p. 206.)

### Non-crystallising Printing Compositions. E. E. Beard and Du Pont. (IX, p. 210.)

## VI—FIBRES; YARNS; FABRICS

### Macromolecular Chemistry and Textiles. G. Champetier. *Teintex*, 13, 277–285, 325–327 (Aug. and Sept. 1948).

These papers record the proceedings of a Conference organised by the Institut Textile de France to discuss the structures of natural high polymers such as wool and cellulose, in which a résumé of the work of Staudinger, K. H. Meyer, and K. H. Mark with their collaborators is given; also of artificial fibres such as the rayons, and of synthetic textiles such as nylon. The treatment is descriptive of available knowledge. H. H. H.

### Certain Variations in the Structure and Properties of Natural Cellulose Fibers. E. E. Berkley. *Text. Research J.*, 19, 363–367 (June 1949).

### New Method of Evaluation of the Crystallite Orientation of Cellulose Fibers from X-ray Data. P. C. Tsien. *Text. Research J.*, 19, 330–341 (June 1949).

### Autoxidation of Alkali Cellulose. D. Entwistle, E. H. Cole, and N. S. Wooding. *Text. Research J.*, 19, 609–624 (Oct. 1949).

### Preparation and Properties of Mechanically Modified High Polymers. E. Steurer. *Melliand Textilber.*, 29, 127–130, 169–170 (April and May 1948).

The comminution of high polymers in an oscillating ball mill is accompanied by both depolymerisation and deformation of the macromolecules. Changes in molecular arrangement have been investigated by measurements of thermal expansion, heat of wetting, and X-ray diffraction; and changes in degree of polymerisation (D.P.) by measurements of viscosity and osmotic pressure. X-ray analysis shows that the diagram for cellulose changes on grinding towards that of the amorphous material, but that on wetting with water recrystallisation takes place and the diagram of cellulose hydrate appears. Recrystallisation of ground cellulose derivatives and polyamides can be induced by heating to a temperature within a narrow range which depends on their chemical constitution. Curves are given for the volume change of various polymers as a function of temperature; these show that there is a volume contraction over a temperature range which is specific for each substance. The heat of wetting of cellulose hydrate is increased by grinding. The disorientation caused by even prolonged grinding is not complete, for the samples show residual double refraction and their temperatures of recrystallisation are far below their melting points. This indicates a disorientation of molecular segments rather than of whole molecules. A graph shows how the viscosity of cellulose decreases with increasing duration of grinding. Extrapolation of the results shows that a limit to the degradation is reached at a D.P. of 27. The curve showing the rate of decrease of viscosity of cellulose on heating to  $150^\circ\text{C}$ . is similar to that showing the rate of decrease on grinding, but the composition of the degradation products is different. The carbon content of the ground samples remains unchanged, whereas that of the heated samples increases. Other evidence confirms that the degradation caused by grinding is not due to thermal decomposition. F. A.

### The "Subcutis" and other Cuticular Preparations from Wool and Hair. E. H. Mercer, J. Lindberg, and B. Philip. *Text. Research J.*, 19, 678–685 (Nov. 1949); *Melliand Textilber.*, 31, 32–35 (Jan. 1950).

Evidence for the existence of a "subcutis" in wool fibres described by Reumuth (Dissertation, Aachen, *Forschungsheft 3 d. Deutsch. Forsch.-Inst. f. Text.-Ind.*, München-Gladbach (1938)) has been examined. It is concluded that three components may be recognised in the cuticle of wool and hair—the endocuticle, exocuticle, and epicuticle. The last component, although very thin, is very resistant chemically. The intermediate protein layer differs considerably from the keratin of the cortex and endocuticle. By dissolving the keratin the epicuticle can be separated as a continuous tube, the external surface of which is that of the original fibre. P. C.

### Fine Histology of the Keratin Fibres. J. Lindberg, E. H. Mercer, B. Philip, and N. Gräfén. *Text. Research J.*, 19, 673–678 (Nov. 1949).

A summary of the recent work on the fine histology of keratin fibres is presented as revealed by recent optical and electron microscopy. The complex structure of the cuticle is described. The practical importance of the new work is discussed in relation to diffusion phenomena (dyeing) tests for damage in wool, Allwörden's reaction, and shrinkproof treatments. The need for a definite terminology for the new components is emphasised. P. C.

### Evidence of Chain Folding in a Synthetic Polypeptide and in Keratin. E. J. Ambrose and W. E. Hanby. *Nature*, 163, 483–484 (26th March 1949).

A polypeptide has been prepared by the polymerisation of the *N*-carboxylic anhydride of  $\gamma$ -methyl L-glutamate. This polymer was insoluble in the usual organic solvents, but it dissolved readily in formic acid and slowly in *m*-cresol. Its specific viscosity in *m*-cresol corresponded to mol. wt. 30,000. Polarised infra-red observations indicate that it has a folded structure similar to that of  $\alpha$ -keratin. It is likely that this folding results from the steric hindrance to inter-chain hydrogen-bonding produced by the bulky side-chains. A. S. F.

**Measurement of Friction between Single Fibres.**

**IV—Influence of Various Oxidising and Reducing Agents on the Frictional Properties of Wool Fibres.** J. Lindberg and N. Gralén. *Text. Research J.*, 19, 183–201 (April 1949).

The twist-friction meter previously described (J.S.D.C., 65, 136 (March 1949)) has been modified to enable fibres to be treated when they are inserted in the instrument, thus avoiding damage due to the excessive handling and abrasion that occur if mounted after treatment. Using this method the effect of various oxidising and reducing agents on the frictional properties of wool fibres has been studied. The frictional behaviour of wool and its change on treatment is explained in terms of the histological structure of the outer layers of the wool fibre. P. C.

**Xanthation of Alkali Cellulose—III.** K. Hess and H. Hepp. *Melliand Textilber.*, 29, 305–310, 343–348 (Sept. and Oct. 1948).

Xanthation of alkali cellulose at ordinary temperatures takes place in the amorphous regions of the fibres, the X-ray interference diagram of the material remaining unchanged. Thermostable alkali cellulose, prepared at above 60°C. in 30–35% NaOH, was xanthated at elevated temperatures, when the reaction was found to take place in the micellar regions and was followed by X-ray methods. Results are given for the degree of xanthation of these two types of alkali cellulose as a function of time and temperature. F. A.

**Rayon Staple Fibre.** H. Böhringer. *Melliand Textilber.*, 29, 255–258, 289–294 (Aug. and Sept. 1948).

The production of staple fibre, particularly viscose, is described, and the relation between its properties and application in the spinning of various types of yarn is discussed with special reference to the harmful effects of tension. Many properties of viscose staple and other fibres are compared. F. A.

**Formaldehyde Curing of Zein Fibres.** C. D. Evans and C. B. Croston. *Text. Research J.*, 19, 202–211 (April 1949).

The curing of zein fibres by formaldehyde has been studied, which has led to the development of a continuous two-stage process. The first stage consists of a mild cure which introduces 0.75% formaldehyde into the fibre. This fibre on stretching has improved strength and elasticity. The second stage introduces a further 3% formaldehyde and stabilises the length of the fibre. Curing occurs only under acid conditions, and ammonium salts catalyse the reaction. When cured below pH 0 the fibres are stable to both acid and alkaline boiling. P. C.

**Influence of Water on the Tensile Properties of Glass Fibre.** H. Driesch. *Melliand Textilber.*, 29, 375–377, 412–417 (Nov. and Dec. 1948).

The influence of water on the tensile properties of glass fibre has not previously been reported. A description is given of testing methods which have now been employed to show that water treatment may cause a decrease in strength and increase in extensibility. The changes take place very rapidly when the fibres are placed in water, and are complete in 15 min. The extent of the change increases with increase in the specific surface of the fibres. Glass fibres of low alkali content show an increase in extension but no change in strength. F. A.

**Textile Chemistry and Physiology—II.** O. Mecheels. *Melliand Textilber.*, 30, 553–557 (Dec. 1949).

Following a previous paper (*ibid.*, 30, 1 (Jan. 1949)), the results of experiments are described illustrating methods of assessing the effect of structure of textiles on their physiological properties, particularly as regards the influence of different types of dyeing and finishing processes. B. K.

**Old Peruvian Fabric.** G. Wilhelmi. *Melliand Textilber.*, 29, 422 (Dec. 1948).

A description is given of a dyed animal-fibre fabric discovered in Peru and dating from about A.D. 1200. F. A.

**Comparison of Viscose Staple Fibre Fabrics.** O. Heimeran. *Melliand Textilber.*, 29, 340–342, 378–381 (Oct. and Nov. 1948).

An extensive series of investigations on the influence of manufacturing and finishing conditions on the utility value of viscose staple fibre fabrics is briefly summarised. F. A.

## PATENTS

**Cellulose Acetate Fibres having Affinity for Acid Dyes.** J. W. Fisher, H. Bates, and E. W. Wheatley. B.P. 630,528.

Fibres made from a mixture of cellulose acetate and acylated poly-4-amino-1:2:4-triazole have a good affinity for acid dyes when aftertreated with caustic soda; e.g. a solution of cellulose acetate in formic acid is added to a solution of poly-4-amino-octamethylene-1:2:4-triazole (from sebacic dihydrazide and hydrazine) in hot formic acid, and the mixture poured into water. The white fibrous mass is dried, dissolved in acetone, and spun into fibres. The resulting yarn is then immersed in 4% caustic soda for 3 min. at 50–60°C. and carefully rinsed free from alkali. W. G. C.

**Stretching Cellulose Acetate Yarn.** T. B. Frearson and E. A. Goodall. B.P. 630,390.

The uniformity of the denier is improved by prestretching cellulose acetate yarns in their unsoftened state by 60–75% of their extensibility and then stretching the yarns in steam above 100°C. W. G. C.

**Linear Polythioesters.** Wingfoot Corp. B.P. 630,625.

Polymers which are more stable and of higher m.p. than similar products made from glycols and dibasic acids are obtained by treating dithiols with the acid chloride of a dibasic acid, e.g. pentamethylenedithiol and terephthaloyl chloride. The products are made into fibres which can be cold-drawn. W. G. C.

**Felt Manufacture.** Sylvania Industrial Corp. B.P. 630,666.

A felt lap is prepared by carding or air-blowing on to a moving band a mixture of non-adhesive and potentially adhesive fibres, e.g. wool, cellulose, or mineral fibres on the one hand and any extruded potentially adhesive substance on the other. The mat is made coherent by localised adhesion of the components, e.g. by passing between heated calendars which are heavily embossed in the requisite pattern. J. W. B.

**VII—DESIZING; SCOURING; CARBONISING; BLEACHING**

**Relation between the Structure and Cleansing of Fibres.** H. Staudinger. *Melliand Textilber.*, 29, 302–305 (Sept. 1948).

The structures of natural and synthetic fibres are compared. Mechanical inclusion of foreign matters inside fibres is of interest to the laundry and dry-cleaning industries. Such inclusion can be demonstrated by replacing the water in fibres first by a water-soluble organic compound and then by a water-insoluble compound. In this way fats, oils, and fatty acids were incorporated in fibres. F. A.

**VIII—DYEING**

**Solubilisation of Dyestuffs with Surface Active Agents.** American Association of Textile Chemists and Colorists, Midwest Section. *Amer. Dyestuff Rep.*, 38, P 728–P 732 (3rd Oct. 1949).

Surface-active agents serve as true solubilising agents for a number of cellulose acetate rayon and acid dyes. Micelle formation will explain this phenomenon, and hence, beyond a critical point, increased detergent concentration results in greater solubilisation. Salts lower this critical concentration. Experiments on nylon staple indicate that there may be an optimum solubility range of the dye which will give the best dyeing properties. Greater solubility exerts too great a retarding effect and lesser solubility causes unevenness. It is suggested that a comprehensive study of solubilisation may be a help in determining the dyeing properties of new fibres. A. S. F.

**Preliminary Study of Variables in Padding.** American Association of Textile Chemists and Colorists, New York Section. *Amer. Dyestuff Rep.*, 38, P 159–P 171 (21st Feb. 1949).

The effects of such factors as padder characteristics, distribution of pressure, load, temperature, fabric speed and construction, and wetting agents, on the pick-up of liquor during padding are described graphically. A. S. F.



**Absorption of the Two Vat Dyes Caledon Red BN and Caledon Jade Green by Cotton.** A. Geake. *J. Textile Inst.*, 40, T 57-T 87 (Jan. 1949).

The absorption by scoured cotton yarn of two anthraquinonoid vat dyes in presence of sodium hydrosulphite and sodium hydroxide has been studied as a function of time and at equilibrium. The effect of pyridine on the activity coefficients of Caledon Jade Green B (C.I. 1101) was measured by examining the redox potential of the leuco dye-oxidised dye system. Full details for measuring absorption isotherms in presence of nitrogen, and for estimating dye concentrations in solution and on the fibre, are described. The chief variables studied in the absorption measurements were concentrations of dye and sodium sulphate, in presence of a constant concentration of sodium hydroxide. The rate of dyeing, and possibly the equilibrium absorption, were reduced by soaking the cotton, prior to dyeing, in water or dilute aqueous solutions. A number of data on the spectral characteristics of solutions of the purified dyes in various solvents are recorded.

A. S. F.

**Dyeing of Rayons of Different Denier.** L. Schwabe. *Textil-Praxis*, 4, 629-631 (Dec. 1949).

Differences in apparent depth of hue of two rayons of different denier when dyed under identical conditions are due to a variety of factors, e.g. relationship between the crystalline and amorphous portions of the fibre, surface structure of the fibre, and refractive index of the dyed fibre. A nomogram is given to estimate the amount of dye required to give the same depth on rayons of different denier.

B. K.

**Dyeing of Nylon.** J.-P. Niederhauser. *Textil-Rund.*, 4, 442-453 (Dec. 1949).

After reviewing the literature dealing with the dyeing of nylon, the results of experiments are described on the effect of chemical constitution, especially degree of sulphonation, on the affinity of acid dyes for nylon in both self and combination shades. A selection of dyes is given for the production of solid shades on wool-nylon unions and for the reservation of the latter fibre. Eulan N (IG), Eulan CN (IG), and Mitin FF (Gy), which are colourless synthetic mothproofing agents, can be used to improve the degree of reservation of the nylon by blocking the amino groups in the latter fibre, so that the dye is taken up by the wool.

B. K.

**Behaviour of Acid Dyes on Nylon.** K. Anacker. *Melliand Textilber.*, 29, 348-350 (Oct. 1948).

The absorption by nylon of some acid dyes including monosulphonates and disulphonates has been measured. The monosulphonates are the more strongly absorbed and may displace previously applied disulphonates.

F. A.

**How Hair Dyes Work.** F. Winter. *Amer. Perfumer Essent. Oil Rev.*, 53, 138-140; 54, 213-215 (1949); *Chem. Abs.*, 43, 9386 (25th Nov. 1949).

The effects produced by and the use of *p*-tolylene-diamine, pyrogallol, *o*-aminophenol, Metol, diamino-phenols, sulphaaminophenol, *p*-aminodiphenylamine, 1:4-diaminodiphenylamine, sulpha-1:4-diaminodiphenylamine, and nitrated aniline derivatives are described. Recipes, developers, contact times, and resulting hues are given.

C. O. C.

**Chemistry of Fur Dyes.** A. Ginzel. *Melliand Textilber.*, 29, 384-385 (Nov. 1948).

A review is given of the probable course of the reactions which take place when oxidation dyes are applied to furs.

F. A.

**Aftertreatment of Sulphur Dyeings with Fixer DCM.** S. Rakhlina. *Tekstil. Prom.*, 9, 29-32 (March 1949).

Fixer DCM, the copper derivative of the dicyandiamide-formaldehyde condensate DCU, is rapidly taken up by sulphur dyeings at 75°C., the amount absorbed being directly proportional to the strength of the dyeing. Fastness to light and wet treatments is improved. The same effect is obtained by using a mixture of DCU and a copper salt.

A. E. S.

## PATENTS

**Dyed Corrosion-resistant Coatings on Zinc and High Zinc Alloys.** E. R. McLean, D. M. Jenkins, and Clark Thread Co. *U.S.P.* 2,477,310.

The metal is treated with an aqueous solution containing a  $\text{Cr}_2\text{O}_3$ -containing compound, lactic acid and/or soluble

lactates, and a mineral acid. The solution is maintained at pH 1.0 and contains per litre 150 g.  $\text{Cr}_2\text{O}_3$  and 1-9 g. lactic acid. The metal is then washed, dyed while still wet, dried, and finally cured or heated to fix the film and the dye on the surface of the metal. A list of suitable dyes includes among others C.I. 5, 57, 179, 184, 430, 698, 714, 735, 1034, 1054, and 1078.

C. O. C.

**Aqueous Baths for Colouring Stainless Steel.** D. J. Clini and Heatbath Corp. *U.S.P.* 2,476,700.

Stainless steel is coated black by heating it in a bath containing a hydroxide (80 parts by weight), permanganate (2), sulphide (3), and sulphate (1), the metal in each component being an alkali metal, and sufficient water to give the liquor b.p. 250°F.

C. O. C.

## IX—PRINTING

**Printing of Direct Dyes.** A. G. Barinova and K. V. Komlev. *Tekstil. Prom.*, 9, 22-24 (Aug. 1949).

In the application of the fixing agent DCU (dicyandiamide-formaldehyde condensate) and copper salts to the production of fast prints of direct dyes, copper may be introduced into the print paste as a soln. of cupric oxide in a mixture of aqueous caustic soda and glycerol, DCU being applied to the print after ageing by padding; or DCU may be added in the cold to a neutral printing paste of direct dye, the aged print being padded in copper acetate soln. The concn. of dye attainable is lower by the second method.

A. E. S.

**Fundamental Study of Aging Conditions in the Vat Ager.** F. Fahnoe. *Amer. Dyestuff Rep.*, 38, 663-672, 685 (19th Sept. 1949).

The variables studied in this work were the initial moisture contents of the cloth and of the dye paste, R.H. of the atmosphere, the temperature, steam quality, and air content in the ager, and rate of steam flow. A small experimental ager to which thermocouples and other measuring devices were attached was used, and it is shown that vat agers are capable of providing constant operating conditions, regardless of external conditions, if adequate instrumentation is employed.

A. S. F.

**Picture Printing in Ancient Mexico.** P. Westheim. *Ciba Review*, (70), 2581, 2582 (Sept. 1948).

The printing of pictures and designs by means of small rectangular slabs a few inches long or small brick cylinders was common in Mexico before the arrival of Europeans. They were used for printing both fabrics and ceramics but above all for cosmetic purposes, all classes of society using them for printing designs on their faces, arms, legs, and bodies.

C. O. C.

**Removal of Printing Thickeners from Fabrics.** N. E. Fedorova and E. I. Sheludyakova. *Tekstil. Prom.*, 9, 31-34 (July 1949).

Diazonium salts are printed in starch thickening on naphtholated fabric, and the starch retained after washing is determined. Removal of starch is facilitated by the presence of free fatty acids in the thickening. These form soaps with the caustic soda present in the first wash-liquor, which should contain also sodium carbonate in order to prevent the formation of lime soaps. The temperature should not be < 70°C.

A. E. S.

## PATENTS

**Non-crystallising Printing Compositions.** E. E. Beard and Du Pont. *U.S.P.* 2,476,952.

Lacquer-type printing pastes for textiles and printing inks for paper with no tendency to crystallise comprise copper phthalocyanine and metal-free phthalocyanine, a tin phthalocyanine (1-12% on the weight of the copper phthalocyanine), and a liquid aromatic hydrocarbon which has a tendency to encourage crystal growth in copper and metal-free phthalocyanines.

C. O. C.

**Sensitised Sheets for Positive Diazotype Screen Reflectography Processes.** Chemische Fabrik L. Van der Grinten. *B.P.* 630,874.

**Correcting the Colour Balance in Colour Photography.** Kodak Ltd. and M. L. Dundon. *B.P.* 631,873.

**Mechanisation of Screen Printing.** J. Sieger. (I, p. 203.)



## X—SIZING AND FINISHING

**Review of Sizing.** H. Gensel. *Melliand Textilber.*, 29, 243-246, 271-272 (July and Aug. 1948).

The sizing of cotton and rayon warps is discussed with particular reference to the use of modified starches, cellulose derivatives, and linseed oil. The machines used for sizing rayon are described. F. A.

**Permanent Cellulose Finish L.** A. A. Kopyev, N. A. Boris, and Z. A. Tolstousova. *Tekstil. Prom.*, 9, 23-25 (June 1949).

Permanent Cellulose Finish L is applied to cellulosic fabrics to impart durable full finishes, which compare favourably with those produced by the more costly cellulose ethers. It is prepared by stirring bleached cotton linters or viscose scrap with sodium zincate soln. in a jacketed iron pan for 1½-2 hr. at -5 to +5°C. The zincate soln. is made by adding 1 part of zinc oxide to 4 parts of 40% caustic soda soln., boiling until clear, and diluting 1:2 with water. The final soln. contains per litre—90-100 g. sodium hydroxide, 20-25 g. zinc oxide, and 15-30 g. cellulose. Fabric is impregnated in this soln. and passed into hot water to precipitate the cellulose. Alternatively, precipitation may be effected by steaming, or by passing through caustic soda soln. of mercerising strength. These methods are preferred to the traditional acid treatment. Dyeing may, with advantage, follow the cellulose treatment, which can replace mercerisation for many purposes. On the basis of laboratory experiments it is suggested that Permanent Cellulose Finish L should be applied to grey fabric and precipitated by treatment in hot water. Kier-boiling should be carried out in the washings (dil. sodium zincate soln.), which are stated to be highly efficient for this purpose, and bleaching and other processes follow in the usual way. A fabric of full, durable finish is obtained in a simple and economical manner. A. E. S.

**Crease-resistance and Cotton.** G. S. Buck, Jr., and F. A. McCord. *Text. Research J.*, 19, 216-247 (April 1949).

A study of the crease-resistance of fabrics with special reference to cotton goods. It is treated from both the economic and technical aspect and covers a review of the market prospects and the various technical considerations such as fibre and fabric structure, application of crease-resistant finishes, and methods of testing crease-resistance. Further topics for research in this field are indicated. There are 165 references to the literature. P. C.

**Pore Size Distribution in Textiles—A Study of Windproof and Water-resistant Cotton Fabrics.**

H. Wakeham and N. Spicer. *Text. Research J.*, 19, 703-710 (Nov. 1949).

An improved method for studying the interfibre and interpore space in fabrics by means of a mercury-pressure porosimeter is described, and the results of measurements on fourteen cloths of tight structure, six of which had been waterproofed, are reported. It is shown that differences in the air permeabilities of fabrics of different weaves can be explained in terms of the results of porosity measurements. It is demonstrated that fibres in water-resistant fabrics swell on exposure to moisture and close the pores of the fabric, thus reducing the passage of water. Definite relationships are considered to exist between pore size and volume on the one hand and air and water permeability on the other. Schematic drawings and photographs of the porosimeter are given. P. C.

**Preservation of Fish Nets.** B. Farrer. *Brit. Columbia Research Council, Tech. Bull.* (11), 72 pp.: *Chem. Abs.*, 43, 8688 (10th Nov. 1949).

A preservative for fishing gear should be bactericidal and protect against abrasion and weathering. Experiments have shown that it is best to apply the bactericide first and then the abrasion-resistant coating. Phenylmercury chloride was the most effective colourless preservative for reducing deterioration due to immersion, and copper naphthenate the most effective coloured preservative. Both require an abrasion-resistant aftercoating. Linseed oil has been used for the coating but it is deleterious, being less so if applied from a volatile solvent. Cutch followed by CuSO<sub>4</sub> in neutral or ammoniacal solution is the only agent which protects linen and light cotton gear against weathering. Fixation with sodium or potassium

dichromate is useless. For heavy cotton web the best treatment is cutch—CuSO<sub>4</sub>—coal tar, which gives protection against bacteria, abrasion, and weathering. A cold dip in coal tar thinned with a volatile solvent and with copper naphthenate added is suitable for lacing twines; treated in this way they are more easily handled than when hot-tarred. C. O. C.

**Reducing the Alkali Solubility of Wool by Formation of New Cross-links.** W. Kirst. *Melliand Textilber.*, 29, 236-240 (July 1948).

In the Harris process for improving the alkali resistance of wool by reduction and treatment with alkylene dihalides it has been suggested that new cross-links of the type -S-R-S- are formed. It was considered doubtful whether this is the sole reaction, and treatment of unreduced wool with alkylene dihalides was found to decrease its alkali solubility. The extent of yellowing in alkali, however, was decreased by the alkylene dihalide treatment only when the latter was preceded by reduction. Results similar to those observed with alkylene dihalides were also obtained using di- or poly-ethyleneimine derivatives. The changes in the properties of wool treated with several such derivatives are given in detail. In a subsequent note on this paper H. Wenderoth (*ibid.*, 29, 350 (Oct. 1948)) quotes references concerning the preparation of 1:6-hexanedithiol bischloromethyl ether and its use for treating wool. F. A.

**Cross-linking in Wool.** E. Elöd and H. Zahn. *Melliand Textilber.*, 29, 269-270 (Aug. 1948).

The type of cross-linkages introduced by treatment of wool with chloromethyl ethers is discussed. The treatment results in a decrease in cystein content, and it is concluded that some sulphur-containing links are involved. F. A.

**Reduction of the Swelling of Regenerated Cellulose Fibres by drying at High Temperatures.**

A. Feubel and F. Hilgers. *Melliand Textilber.*, 29, 233-235 (July 1948).

The density of regenerated cellulose fibres increases and their swelling in water decreases as the temperature of drying of the freshly spun material is increased. Uneven drying thus leads to density variations throughout the fibres, and this effect can be detected by a staining method. A series of freshly spun viscose fibres was dried for 15 min. at different temperatures between 200° and 260°C. The swelling of the fibres decreased progressively as the temperature was increased over this range, but their strength and extensibility decreased. The time of drying at 260°C. was varied, when it was found that the swelling decreased rapidly, but the changes in tensile properties took place more slowly. By drying for 7-8 sec. at 270°C. it was possible to decrease the swelling from 104.6 to 72.1% without affecting the tensile properties. F. A.

### PATENTS

**Coated Cotton Fabric Highly Resistant to Steam for Long Periods.** A. J. Jennings and Du Pont.

U.S.P. 2,477,336.

Cotton fabric coated with natural rubber, polymerised chloroprene, copolymers of isobutylene and a conjugated diolefin, or copolymers of butadiene and vinylbenzene or acrylonitrile and 1-25% (on the total weight of solids) of calcium or magnesium oxide loses no strength when exposed to steam under pressure up to 70 lb./sq. in. for long periods. C. O. C.

**Typewriter Ribbons.** British Celanese Ltd.

B.P. 630,915.

Fabric woven from high-tenacity regenerated cellulose yarns (prepared by stretching and then saponifying an organic ester of cellulose) is shrunk by treatment with an aqueous solution of an alkali-metal hydroxide and then impregnated with a ribbon-inking composition. The treated fabric yields typewriter ribbons which are superior to silk ribbons in their ability to mark off clearly for a long period. C. O. C.

**Knitted Fabric.** S. M. Edelstein.

B.P. 630,846.

A fabric having spaced knitted warp threads, and substantially closed loops extending from one warp thread and interlaced with adjacent knitted warp threads, when tensioned has a hexagonal mesh. This structure is permanently maintained if the fabric is coated with a cellulosic film and kept stretched during drying. G. E. K.

## XI—PAPER AND OTHER CELLULOSIC PRODUCTS

### PATENTS

**Increasing the Wet Strength of Paper.** H. Jackson Ltd. and A. Wexler. B.P. 631,483.

The wet strength of absorbent paper is increased by incorporating into the beater stock 1.6–3.5% (on dry weight of pulp) of a metal hydroxide precipitable in gelatinous or gel-like form (e.g. aluminium hydroxide, produced from aluminium sulphate and sodium aluminate; ferrous or ferric hydroxide, from ferrous sulphate and sodium hydroxide; chromium, zinc, manganese, stannous or stannic, titanium, or magnesium hydroxide) without adding any other wet-strengthening agent. Except when iron, tin, or titanium hydroxide is used the treated paper is heated to 130–140°C., i.e. above the normal temperature of the drying cylinders of the paper machine, to secure additional increase in wet strength. S. V. S.

**Thick Foils of Regenerated Cellulose.** Kooperation Förbundet Förening u.p.a. B.P. 631,260.

Cellulose foils are formed in a precipitating liquid, the final bath containing a cement, e.g. gelatin. After emerging from the bath they are cemented together by e.g. passing together over heated rollers. By laminating before final drying strong and uniform thick foils are produced. J. W. B.

**Manufacture of Cellulose Acetate.** British Celanese Ltd. B.P. 630,937.

Secondary cellulose acetate, which requires no separate stabilising treatment for use in moulding, is produced by ripening the primary acetate in the presence of 3–10% of ammonium bisulphate and 33–45% of water at 90–100°C. for about 12 hr. W. G. C.

**Continuous Esterification of Cellulose.** C. R. Fordyce, C. L. Crane, and Eastman Kodak Co. U.S.P. 2,478,383.

**Cellulose Acetate.** G. A. Richter, L. E. Herdle, and Eastman Kodak Co. U.S.P. 2,478,425.

## XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

**Chemical Constitution and the Tanning Effect.** III—Polyhydroxybenzophenones. A. Russell and G. B. Butler. *J. Amer. Chem. Soc.*, 71, 3663, 3664 (Nov. 1949).

Although maclurin, 3':4':2:4:6-pentahydroxybenzophenone, precipitates gelatin from solution, neither it nor 14 other polyhydroxybenzophenones convert hide to leather as judged by colour, feel, texture, flexibility, and fullness. C. O. C.

**Processes relating to the Woolled Sheep Industry.** W. J. Waldie. *Textile J. of Australia*, 23, 568–576 (20th Sept. 1948).

The processing of woolled sheepskins from the raw to the finished state is described, with emphasis on the effects of the various stages on both the wool and the leather. A detailed description is given of soaking, fleshing, scouring, pickling, tanning (vegetable, alum, and chrome), degreasing, fat-liquoring, drying, dyeing (with cellulose acetate, acid, and fur base dyes), and finishing. A. S. F.

## XIII—RUBBER; RESINS; PLASTICS

### PATENTS

**Resorcinol-Formaldehyde Resins.** Mississippi Valley Research Laboratories Inc. B.P. 630,258.

Resins of greater impact strength and more flex-resistant than the usual phenol-formaldehyde resins are obtained by treating the ether of resorcinol or its derivatives and an organic dihalide with formaldehyde under alkaline conditions, and then heating to harden the material. W. G. C.

**Glycol Dimethacrylates.** Du Pont. B.P. 630,632.

Methacrylate diesters of a mixture of glycols of formula  $\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{H}$  ( $n$  = an integer) and mol. wt. 185–270 can be polymerised to form hard tough sheets and shaped articles. W. G. C.

**Polyallyl Ether Compositions containing an Orthosilicate Ester.** J. R. Roach and General Mills Inc. (III, p. 204.)

## XIV—ANALYSIS; TESTING; APPARATUS

**First Annual Review of Analytical Chemistry.** *Anal. Chem.*, 21, 2–173 (Jan. 1949).

Twenty-nine papers are presented in a comprehensive review of recent progress in fundamental analytical chemistry. The separate subjects reviewed are—Light absorption spectrometry, infra-red spectroscopy, Raman spectra, ultra-violet absorption spectrophotometry, X-ray absorption, X-ray diffraction, emission spectroscopy, mass spectrometry, electron microscopy, light microscopy, polarographic theory, instrumentation and methodology, organic polarography, amperometric titrations, electroanalysis, chromatographic separations, distillation, extraction, ion exchange, nucleonics, indicators, fluorometric analysis, instrumentation, statistics applied to analysis, inorganic microchemistry, organic microchemistry, inorganic gravimetric analysis, organic gravimetric analysis, inorganic volumetric analysis, and volumetric analytical methods for organic compounds. W. K. R.

**Thioacetamide in place of Gaseous Hydrogen Sulphide for Precipitation of Insoluble Sulphides.** H. H. Barber and E. Grzeskowiak. *Anal. Chem.*, 21, 192 (Jan. 1949).

Thioacetamide, a readily available commercial product, which is free from unpleasant odour and forms stable aqueous solutions, has been used successfully in place of gaseous hydrogen sulphide in the qualitative analysis of the cations of Groups II and III. An aqueous solution is added to the solution containing the cations, no great excess being required to bring about complete precipitation of the insoluble metal sulphides. The hydrolysis of thioacetamide gives a relatively low concentration of sulphide ion in solution, favouring the rapid coagulation and filtration of the insoluble sulphides. W. K. R.

**Volumetric Determination of Small Amounts of Iron.** W. D. Cooke, F. Hazel, and W. M. McNabb. *Anal. Chem.*, 21, 1011 (Aug. 1949).

Chromous chloride alone is a satisfactory reducing agent for small amounts (0.1–10 mg.); with larger amounts, the green colour of the chromic ion interferes. W. K. R.

**Indirect Method for Estimation of Sodium in Water Supplies.** J. R. Rossum. *Anal. Chem.*, 21, 190 (Jan. 1949).

The alkalinity and hardness are determined titrimetrically and the diluted conductance is determined by diluting the water sample with cool boiled distilled water so that the conductance is approx. 100 micromhos at 25°C. This value multiplied by the dilution factor is the diluted conductance.

$$\text{Sodium (p.p.m.)} = 0.186x + 0.113(\text{Alkalinity} - 0.46(\text{Hardness}))$$

where  $x$  is the diluted conductance in micromhos and both hardness and alkalinity are expressed in p.p.m. as  $\text{CaCO}_3$ . The method is inapplicable in the presence of high potassium or ammonium concentrations, and outside the pH range 6–9. W. K. R.

**Fatty and Rosin Acid Soaps and their Mixtures—Conductometric and Potentiometric Analysis.** S. H. Maron, I. N. Ulevitch, and M. E. Elder. *Anal. Chem.*, 21, 691–695 (June 1949).

Potentiometric methods are of limited applicability in the analysis of fatty and rosin acids and their soaps, but using a mixture of equal vol. of water and isopropyl alcohol as solvent, reliable results are obtained by conductometric methods. Fatty or rosin acid is determined by direct titration with alkali, and soap by titration with acid. By addition of a known excess of standard acid followed by conductometric titration with alkali, the soap and free acid contents or the soap and free alkali contents of a soap or soap solution may be determined by a single titration. W. K. R.

**Studies in Coaltar Colours, FD&C Yellow No. 6 and C.I. No. 26.** C. Stein. (IV, p. 205.)

**Measurement of Friction between Single Fibres.** IV—Influence of Various Oxidising and Reducing Agents on the Frictional Properties of Wool Fibres. J. Lindberg and N. Gralén. (VI, p. 209.)

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